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HIGH POWER LASER AND MATERIALS INVESTIGATION

MASTER

**FINAL REPORT FOR THE PERIOD
31 JULY 1978 — 28 OCTOBER 1979**

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June 1980

**Work Performed under Contract
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**Defensive
Systems
Division**

95 Canal Street, Nashua, New Hampshire 03061

Prepared For:

**Department of Energy
Nevada Operations Office
Under Contract DE-AC08-78DP40054**

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FINAL REPORT FOR THE PERIOD
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E.P. Chicklis
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SANDERS
ASSOCIATES, INC.

**Defensive
Systems
Division**

95 Canal Street, Nashua, New Hampshire 03061

Prepared for:

The Department of Energy
Office of Inertial Fusion Laser
Under Contract Number DE-AC08-78DP40054

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ABSTRACT

This is a combined study of resonant pumped solid state lasers as fusion drivers, and the development of crystalline optical materials suitable for propagation of the high peak powers associated with laser fusion research.

Solid state (storage) lasers represent the most advanced technology for inertial confinement fusion experiments. Flashlamp pumped solid state lasers, however, exhibit specific deficiencies (low efficiency and high thermal loading) which constrain their application to very low repetition rates. Resonant pumped solid state lasers can exhibit very high conversion efficiencies and very low heat loading. High system efficiencies are feasible using efficient pump sources.

Rare gas halide lasers (RGH) show promise for operating with the energy, PRF and efficiency requirements of advanced fusion drivers. RGH lasers, however, are not storage devices and operate with peak powers well below the requirements for fusion drivers. Storage of the RGH energy in solid state lasers appears a viable technique of overcoming the limitations of both media.

During this period of study the concept of RGH/SS lasers was first demonstrated by the lasing of Tm:YLF at 453nm pumped by the 353nm energy of XeF. Excited state densities of $5 \times 10^{18} \text{ cm}^{-3}$ have been attained and spectroscopic measurements show that up to 60% of the pump energy can be converted into useful stored energy. Alternative lasers and pumping schemes are also discussed. In all cases the potential RGH/SS systems are evaluated in respect to internal efficiency and heat loading.

The materials requirements for advanced laser applications will include high peak and average power propagation together with material availability in large (30cm) apertures with very high optical quality. Applications for materials include active (lasers, faraday rotators) and passive (windows, lenses) components.

Crystalline fluoride materials exhibit certain general and specific properties suited to these applications. Some of the desirable properties of certain crystalline fluoride materials include:

- a. low values of n_2 , the non-linear index of refraction
- b. optical transparency far into the uv
- c. low growth temperature (permitting ease of growth scale)

The materials development effort described was directed at growth investigation, and growth scale-up of crystalline fluoride materials. Most of the work involved the host materials YLF (LiYF_4) and KYF (KY_3F_{10}).

The crystal growth process was scaled to produce 10cm diameter crystals of YLF. The investigation included construction of furnace hot zones, the study of the effects of growth parameter variation, and characterization of fabricated samples.

Other new materials that are described are KYF, $\text{KTb}_3\text{F}_{10}$ and EuF_2 . Samples of these materials were grown and sent to specific DoE laboratories for characterization. The results of these tests are presented.

Improvements in the growth process that were done are described in respect to quality improvement and cost savings.

Finally, the technical milestones achieved during this period of study are assessed in respect to the future objections for laser fusion research.

PREFACE

This is a report of an investigation of resonant pumped solid state lasers as fusion drivers, as well as the development of crystalline optical materials suitable for propagation of the high peak powers associated with laser fusion research. The investigation was funded by the Department of Energy under contract #DE-AC08-78-DP40054, Office of Inertial Fusion. The period covered in this report is 31 October 1978 to 28 July 1979.

Dr. Owen Lewis and Dr. Paul Hoff, Office of Inertial Fusion, were technical monitors to this program.

These studies were performed by the Advanced Technology Department, Defensive Systems Division of Sanders Associates, Inc. The Crystal Physics Laboratory, Department of Electrical Engineering and Center for Materials Science, Massachusetts Institute of Technology served as Subcontractor. The program Folweiler was principal investigator at Sanders and the program managers for this program were Mr. Robert Folweiler and Mr. Evan Chicklis. Mr. James Baer and Mr. Mark Knights conducted the study of rare gas halide pumped solid state storage lasers. Mr. Folweiler was assisted by Mr. Thomas Pollak in the crystal growth development. Technical functions of crystal growth, fabrication and optical analysis at Sanders were done by Philip Foley and Leo Terrenzio.

The work at the Crystal Physics Laboratory was under the direction of Dr. A. Linz, and includes growth of new materials, feed synthesis and spectroscopy. Mr. David Gabbe performed the crystal growth, and the feed material process development and synthesis. Dr. Hans Jenssen performed the spectroscopic measurements.

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

TABLE OF CONTENTS

Page

1.0 INTRODUCTION

1.1 High Power Solid State Laser Investigation

1.1.1 Background

1.1.2 Program Objectives

1.1.3 Program Results

1.2 Materials Investigation

1.2.1 Background

1.2.2 Program Objectives

1.2.3 Program Results

2.0 LASER INVESTIGATION

2.1 XeF Pumped Tm:YLF

2.1.1 Tm:YLF Oscillator Experiment

2.1.2 Stimulated Emission Cross Section

2.1.3 Intramanifold Spectroscopy

2.1.4 Fluorescent Lifetimes

2.1.5 Absorption Coefficients

2.1.6 Heat Loading Experiment and Modeling

2.1.7 UV Transmission

2.1.8 Damage Testing

2.1.9 YLF Properties

2.1.10 Sample Growth

2.1.11 System Evaluation

2.2 XeF Pumped Tm:KYF

2.2.1 Laser Experiments

2.2.2 Stimulated Emission Cross Section

2.2.3 Fluorescent Lifetimes

2.2.4 Absorption Coefficient

2.2.5 Known KYF Properties

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LH FOLIO (EVEN)

CLASSIFICATION

RH FOLIO (ODD)

PUBLICATION NO.

CLASSIFICATION

PUBLICATION NO.

TABLE OF CONTENTS
(cont.)

Page

2.3	XeF Pumped Nd:YLF	42
2.3.1	Fluorescence Lifetimes	42
2.3.2	Absorption Coefficient	46
2.4	Other XeF Pumped Systems	48
2.4.1	Yb:YLF	49
2.4.2	Er	49
2.4.3	Ho:YLF	49
2.4.4	Dy:YLF	50
2.4.5	Tb:YLF	53
2.4.6	Gd:YLF	59
2.4.7	Eu:YLF	59
2.4.8	Sm:YLF	59
2.4.9	Pr:YLF	59
2.4.10	Ce:YLF	60
2.5	KrF Pumped Ho:YLF	60
2.5.1	Absorption	60
2.5.2	Emission Wavelength and Lifetimes	62
2.6	KrF Pumped Nd:YLF	64
2.7	KrF Pumped Tb:YLF and Tb:KYF	64
2.8	Other KrF Pumped Systems	70
2.8.1	Yb	70
2.8.2	Tm	70
2.8.3	Er	70
2.8.4	Dy	71
2.8.5	Gd	71
2.8.6	Eu	71
2.8.7	Sm	73
2.8.8	Pr	73
2.8.9	Ce	73

— LOWER LIMIT FOR TEXT

LH FOLIO (EVEN)

CLASSIFICATION

RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

TABLE OF CONTENTS
(cont)

Page

2.9 XeCl Pumped Systems 73

2.10 Fluorescer Systems 73

3.0 MATERIALS 76

3.1 Crystal Growth of Fluoride Materials 76

3.2 Size Scaling of Crystal Growth of RE:YLF 78

3.2.1 Summary 78

3.2.2 Growth Scale of 65mm Diameter YLF Crystals 80

3.2.2.1 Hot Zone Design 80

3.2.2.2 Growth Parameters 80

3.2.2.3 Results of Crystal Growth 83

3.2.3 Crystal Growth of 100mm Diameter Fluoride Crystals 83

3.2.3.1 Hot Zone Design 83

3.2.3.2 Seed Rod Assembly 88

3.2.3.3 Growth Parameters 90

3.2.3.4 Results of 100mm Diameter Crystal Growth Experiments 90

3.2.4 Discussion 93

3.3 Crystal Growth of KYF 98

3.3.1 Introduction 98

3.3.2 Material Preparation for Crystal Growth 99

3.3.2.1 Powders 99

3.3.2.2 Atmosphere 102

3.3.3 Crystal Growth of KYF 102

3.3.4 Zone Refining of KY_3F_{10} 113

3.3.5 Discussion of Results 115

3.4 Process Improvements 117

54 Limit LOWER LIMIT FOR TEXT

LH FOLIO (EVEN)

CLASSIFICATION

RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

TABLE OF CONTENTS
(cont)

Page

3.5 New Materials 119

3.5.1 Introduction and Review of Previous Work 119

3.5.2 Investigation of the $KF-TbF_3$ 122

3.5.3 Europium Difluoride 127

3.6 Properties of YLF and KYF 133

3.6.1 dn/dT for YLF 133

3.6.2 Properties of KYF 133

4.0 CONCLUSION 136

APPENDIX A 140

APPENDIX B 142

DO NOT TYPE BEYOND THIS LINE

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LOWER LIMIT FOR TEXT

LH FOLIO (EVEN)

CLASSIFICATION

RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

LIST OF FIGURES

Figure	Title	Page
1	Resonantly Pumped Tm:YLF Oscillator Geometry	8
2	Tm:YLF Resonator, Energy Storage at Threshold	9
3	Pump and Active Volume Overlap	10
4	Spot Size and Pulsewidth	13
5	Tm:YLF D_2 Cross Section	14
6	Tm:YLF D_2 Cross Section	15
7	Tm:YLF Energy Levels	17
8	D_2 Initial Lifetime Versus Concentration	20
9	Absorption Spectrum of Tm:YLF	21
10	Thermistor Bridge Circuit	23
11	Tm:YLF Energy Flow	25
12	Tm:YLF Energy Flow	27
13	Calibration Curve	29
14	Calibration Curve	30
15	Impurity Absorption Spectra	31
16	Tm:KYF D_2 Cross Section	38
17	D_2 Initial Lifetime Versus Concentration	40
18	Coincidences of Tm:KYF Absorption with XeF Laser Lines	41
19	Nd:YLF Emission Spectrum Pumped 360nm	44
20	$D_{3/2}$ Initial Fluorescent Lifetime	45
21	Nd:YLF Absorption of XeF Output	47
22	Dy:YLF Absorption, 353nm Region	51
23	Dy:YLF Absorption, 353nm Region	52
24	Fluorescence Measurement Using OMA	54
25	Dy:YLF Fluorescence, XeF Pumped	55
26	Tb:YLF Absorption, 353nm Region	56
27	Tb:YLF Fluorescence, XeF* Pumped	57
28	Tb:YLF Fluorescence, XeF* Pumped	58
29	Ho:YLF Absorption, 248nm Region	61
30	Limit of Fluorescence Lifetime Measurement	63

LH FOLIO (EVEN)

CLASSIFICATION

RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

LIST OF FIGURES
(cont)

Figure	Title	Page
31	KrF* Pumped Fluorescence, 2% Ho:YLF	65
32	KrF* Pumped, 248nm Fluorescence	66
33	Absorption 248nm Region (Nd:YLF (unpolarized))	67
34	Tb:YLF Absorption, 348nm Region	68
35	Absorption, 248nm Region Dy:YLF (π)	72
36	Tm:YLF - XeBr* Spectra	75
37	Crystal Growth System	77
38	100mm Diameter Crystal of Er:YLF During Growth	79
39	Hot Zone for Crystal Growth of 70mm Fluoride Crystals	81
40	Effect of Growth Parameters on Interface Shape and Circulation in Melt	82
41	Boule #554 5% Tm:LiYF ₄	84
42	Boule #555 5% Tm:LiYF ₄	85
43	Furnace Arrangement for 100mm Fluoride Crystals	87
44	Seed Holder for Growth of 100mm Fluoride Crystals	89
45	100mm Diameter Crystal of Er:YLF During Growth	91
46	Boule #563b 4% Er:LiYF ₄	92
47	Crystalline Boules of Rare Earth Doped LiYF ₄	95
48	Possible Furnace Assembly for BSS	97
49	Experimental Fluoride Crystal Growth System	100
50	Boule #556 5% Tm:KY ₃ F ₁₀	105
51	Boule #557 5% Tm:KY ₃ F ₁₀	106
52	Boule #560 1% Tm:KY ₃ F ₁₀	108
53	Boule #561 5% Tm:KY ₃ F ₁₀	109
54	Boule #562 5% Tm:KY ₃ F ₁₀	111
55	Boule #567 KY ₃ F ₁₀	112
56	Boule #569 KY ₃ F ₁₀	114
57	Phase Diagram for the KF - TbF ₃ System	128

54 Limit LOWER LIMIT FOR TEXT

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LH FOLIO (EVEN)

CLASSIFICATION

RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

LIST OF TABLES

Table	Title	Page
I	$\partial n / \partial T$ of LiYF_4	33
II	Thermal Comparison: Flashlamp Pumped Glass and XeF Pumped Im:YLF	36
III	Comparison Im:KYF and Im:YLF	43
IV	Potassium Carbonate, Ultrex	101
V	Summary of Crystal Growth of KY_3F_{10}	103
VI	Change in the Refractive Index as a Function of Temperature Between 5° and 50° for YLF and Other Laser Hosts	134
VII	Properties of KYF (Ky_3F_{10})	135

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LH FOLIO (EVEN)

CLASSIFICATION

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PUBLICATION NO

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1.0 INTRODUCTION

1.0 INTRODUCTION

This final report describes the work performed by Sanders Associates for the Department of Energy under contract #ED-78-C-08-1575 High Power Laser and Materials Investigation. The objectives of this program were to investigate and evaluate the use of resonant pumped solid state lasers as laser fusion drivers, and conduct research and development on crystalline optical materials suitable for propagation of the high peak powers associated with laser fusion research.

1.1 HIGH POWER SOLID STATE LASER INVESTIGATION

1.1.1 Background

Solid state (storage) lasers represent the most advanced technology for inertial confinement fusion experiments. Flashlamp pumped solid state lasers, however, exhibit specific deficiencies (low efficiency and high thermal loading) which constrain their application to very low repetition rates. Resonant pumped solid state lasers can exhibit very high conversion efficiencies and very low heat loading. High system efficiencies are feasible using efficient pump sources.

Rare gas halide lasers (RGH) show promise for operating with the energy, PRF and efficiency requirements of advanced fusion drivers. RGH lasers, however, are not storage devices and operate with peak powers well below the requirements for fusion drivers. Storage of the RGH energy in solid state lasers appears a viable technique of overcoming the limitations of both media.

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The overall objectives of this part of the program were to identify and experimentally demonstrate RGH pumped solid state storage lasers and to investigate their suitability as fusion drivers. The specific requirements for such systems include resonant absorption of efficient RGH pumps by a metastable level which could operate with high extraction efficiency and very low heat loading. A further requirement was to choose a host medium for this investigation with properties (low n_2 , high damage resistance, and scalable growth) suited to the eventual application.

1.1.2 Program Objectives

The specific work elements of this program were as follows:

- a. Spectroscopic investigation of RE^{3+} crystalline solids for application as RGH pumped storage lasers
- b. Experimental demonstration of RGH pumped solid state storage lasers and measurement of the relevant spectroscopic properties
- c. Measurement of the thermal loading in promising RGH pumped systems
- d. Performance analysis of promising systems

1.1.3 Program Results

Highlights of this section of the program were:

- Demonstration of lasing at 453nm in XeF pumped Tm^{3+} :YLF. Excited state densities of $5 \times 10^{18} \text{ cm}^{-3}$ have been attained and spectroscopic measurements show that up to 60% of the pump energy can be converted into useful stored energy.

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CLASS 2 TION

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PUBLICATION NO.

• Thorough investigation of the Nd:YLF and Ho:YLF systems.

• A search of most of the trivalent rare earths in YLF and KYF for new candidate systems.

• Analysis of the RGH resonantly pumped system, and its application to XeF pumped Tm:YLF for both efficiency and heat loading.

1.2 MATERIALS INVESTIGATION

1.2.1 Background

The materials requirements for advanced laser applications will include high peak and average power propagation together with material availability in large (30cm) apertures with very high optical quality. Applications for materials include active (lasers, faraday rotators) and passive (windows, lenses) components.

Crystalline fluoride materials exhibit certain general and specific properties suited to these applications. Some of the desirable properties of certain crystalline fluoride materials include:

- low values of n_2 , the non-linear index of refraction
- optical transparency far into the uv
- low growth temperature (permitting ease of growth scale)

The materials development effort on this program was directed at growth investigation, growth and growth scale-up of crystalline fluoride materials. Most of the work involved the host materials

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PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

LiYF_4 (YLF) and KY_3F_{10} (KYF).

These materials are of specific interest because they exhibit the desirable general properties of fluoride crystals and they contain a natural rare earth site which permits the inclusion of active ions (RE^{3+}) for a variety of specific applications.

1.2.2. Program Objectives

Specific program objectives were to:

- Develop growth parameters and fabricate 100mm diameter single crystals of RE:YLF
- Develop growth parameters and fabricate single crystal KYF
- Determine pertinent properties of YLF and KYF
- Investigate the crystal growth of EuF_2
- Develop the phase diagram for KF-TbF_3 , concentrating in the composition range of 25-50 mole % KF
- Investigate promising new possible laser materials
- Evaluate process improvements for crystal growth application
- Provide laser crystal samples for the high power laser investigation.

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PUBLICATION NO.

1.2.3 Program Results

Highlights of this section of the program were:

- Growth of 100mm diameter single crystal RE:YLF. This involved scaling of furnace hardware and growth parameters.

- Growth of several KYF crystals. Low yields were obtained, but several clear, homogeneous, single crystal samples were fabricated. A laser sample, 5mm x 5mm x 20mm was fabricated.

- The KF-TbF₃ system was investigated and it was determined that the cubic phase nominally, KTb₃F₁₀ exists as a solid solution with a formula K_{1+x}Tb_{3-x}F_{10-2x}, from KF composition between 27 to 40 mole percent.

- The optimal composition for crystal growth of KTb₃F₁₀ is 27 mole percent KF.

- A process to reduce europium trifluoride to difluoride was developed, although complete conversion was not obtained, it appears only to be reaction-time limited.

- Crystal growth of EuF₂ was investigated. Flux growth was attempted employing MgF₂ and LiF as the flux material. Initial results are encouraging, however further work is needed to develop the process.

- Single crystal samples of YLF and KYF grown during this program were supplied to a number of universities and government laboratories for property measurements.

- The two photon absorption coefficient (β) of YLF was measured at Harvard University (1). β for YLF was undetectable,

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CLASSIFICATION

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$\leq 4 \times 10^{-6}$ cm/MW, at 266nm. These results indicate that YLF displays potential as window material for uv applications ().

- $\Delta n/\Delta T$ for YLF was measured at the University of Rochester Laboratory for Laser Energetics. At the wavelengths measured, YLF was comparable to other laser host materials.

- Physical properties of KYF were measured at the University of Rochester and are presented in the text.

- Samples of KYF were delivered to the Materials Science Department of Honeywell Corporation for hot forging evaluation.

• Improvements in the hydrofluorination process were made, reduction in cycle time as well as improvements in the process control system has enhanced the efficiency of the purification process.

• Several single crystal and polycrystalline samples were fabricated and used in the laser investigation.

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CLASS 6 ATION

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2.0 LASER INVESTIGATION

2.1 XeF PUMPED Tm:YLF

A major accomplishment of the program was the lasing of Tm:YLF pumped by an XeF laser described in this section. Measurements of this experiment and of the material Tm:YLF have enabled us to characterize the system well.

2.1.1 Tm:YLF Oscillator Experiment

After several design iterations, the short cavity configuration of Figure 1 was constructed. After aligning all elements coaxially with the excimer laser and normal to the axis, the crystal was placed between the two mirrors. In a further refinement, the crystal was mounted in a compact gimbal which could fit in the 8cm resonator.

By scanning a razor blade incrementally across the beam, in both the vertical and horizontal directions, the value of the peak on-axis fluence was derived, along with equivalent spot width and height. This was repeated at small intervals along with the axis of the system.

Using the experimentally derived absorption coefficient for 10% Tm:YLF and the beam profile, the energy deposited on axis as a function of position was calculated. Figure 2 shows this curve, along with the beam width profile. By integrating along the axis, a value of $.44(\text{J}/\text{cm}^2 \text{ on axis})/\text{mJ}$ delivered was arrived at. For instance, if 10mJ are incident on the crystal face, $4.4 \text{ J}/\text{cm}^2$ would be the integrated energy deposited on axis. This, however, was not uniform over the TEM_{00} mode volume of the resonator. Figure 3 shows the overlap of the pump region at its waist with the TEM_{00} mode volume, which was essentially a cylinder of diameter $240\mu\text{m}$. The volume was always overfilled vertically and underfilled horizontally. The effect this had on the lasing characteristics is an unknown.

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RESONANTLY PUMPED Tm:YLF OSCILLATOR GEOMETRY

FL = 127 MM

$R_1 = 0.99+$ AT 454 NM

$R_2 = 0.98$ AT 454 NM

$T = 0.96$ AT 352 NM

$T_1 = 0.83$ AT 352 NM

$T_2 = 0.02$ AT 454 NM

$R_1 R_2 = R = 0.98$

$\delta = 0.01$

4 4% LOSSES PER ROUND TRIP
FROM UNCOATED CRYSTAL FACES

Figure 1

Figure 2

Tm:YLF RESONATOR, ENERGY STORAGE AT THRESHOLD

PUMP AND ACTIVE VOLUME OVERLAP

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Under the best conditions, threshold was reached with 20mJ ϕ delivered to the crystal corresponding to $8.7\text{J}/\text{cm}^2$ absorbed on axis. For 353nm pump photons. This is equivalent to

$$\int N \cdot dL = \int E/h\nu dL = 1.5 \times 10^{19} \text{ cm}^{-2}.$$

The calculation of the resonator losses are relatively straightforward. In a round trip of the resonator, the beam passes through four uncoated crystal faces (3.9% loss, each) and 4.6cm of scattering crystal ($\sim 2\frac{1}{2}\%$ loss), reflects off two mirrors and is partially transmitted by one ($\sim 3\%$ loss), for a round trip logarithmic loss of $\delta = .22$.

If we take these two calculations, ignoring the upper state decay, a lower limit on $\beta\sigma$ can be established by balancing gain against loss as

$$.22 = \delta = g = \frac{1}{2} \int N \cdot dL$$

or

$$\beta\sigma > 7.5 \times 10^{-21} \text{ cm}^2.$$

In Appendix A it is shown that excited state decay can cause the threshold to be measured anomalously high. For the present resonator

$$\tau_D \approx 40 \left(\frac{E_{TH}}{E_p - E_{TH}} \right) \text{ nsec},$$

and at 10% over threshold

$$\tau_D \approx 400 \text{ nsec}.$$

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In the case of 10% Tm:YLF, this corresponds to approximately a 25% increase in the measured threshold. This correction alone would raise the measured value of σ to

$$\beta\sigma \gg 1.0 \times 10^{-20} \text{ cm}^2$$

For the Tm:YLF oscillator, the maximum pulse delay would be 160nsec. The observed delays of 120--150nsec agree with this, increasing the level of confidence in the preceding calculations.

Above threshold, the crystal fluorescence exhibited the expected spatial, spectral and temporal narrowing. Figure 4 shows both the beam pattern and pulsewidth. Although the central spot is the correct size for a TEM₀₀ beam from the resonator, a long streak of reflections, coming from the uncoated and poorly aligned crystal, can be seen. The free running pulsewidth of 45nsec is actually longer than the pump pulse, but is much shorter than the fluorescence lifetime.

Using a J/A 1/2 meter monochromator the wavelength of the emission was measured as 452.59 $\pm$ 0.05nm. No attempt was made to measure the spectral width, but it was obviously less than one nanometer, down from the ten nanometer fluorescence bandwidth.

The output of the Tm:YLF laser is σ polarized. As most YLF lasers, in fact all previously, operate π polarized, this was carefully checked several times.

2.1.2 Stimulated Emission Cross Section

Using a single crystal sample of 1% Tm:YLF the cross-section versus wavelength curve was recorded and quantified for both the π and σ orientations and are shown in Figures 5 and 6. It can be seen that the 452.6nm peak in the σ spectrum is not as high as

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SPOT SIZE AND PULSEWIDTH

SPOT SIZE

Z = 33 CM
W = 0.3 MM

PULSEWIDTH

FW HM = 45 NSEC

$\lambda = 452.6 \text{ nm}$

Figure 4

TM:YLF 1D_2 CROSS SECTION

14

Tm:YLF π

07199-16

Figure 5

TM:YLF 1D_2 CROSS SECTION

15

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Figure 6

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either the σ polarized 449.6nm peak or the π polarized 448.9nm peak.

There is at present no explanation of this discrepancy. There is a possibility that there is an excited state absorption process taking place between 3H_4 and 1I_6 . In the present experiments where a large fraction of the upper state ions decay before the laser pulse begins (See again Appendix A) a large population can build up in 3H_4 (See Section 2.1.6). If such a resonance exists, it could generate large losses, even forcing the lasing to the longer wavelength. The implications of such a resonance on a large efficient machine are not as severe, because, by necessity, a laser that efficiently stores energy in the 1D_2 manifold will limit the number of ions that decay through 3H_4 . The question remains, however, as to whether there would be absorption only below 450nm or merely less absorption above 450nm.

The peak value of the σ curve at 452.6nm of $\beta\sigma = 3.2 \times 10^{-20}$ is within a factor of four of the oscillator derived value of $\beta\sigma = 1.0 \times 10^{-20} \text{ cm}^2$. As unexpected losses should have produced a low oscillator value of $\beta\sigma$, the discrepancy is in the correct direction.

2.1.3 Intramanifold Spectroscopy

Figure 7 shows the revised energy level diagram for Tm:YLF. Using these values and the transition selection rates, the σ polarized transition closest in energy to 452.6nm was identified as shown, starting on the doublet level at 28058 cm^{-1} and terminating on the 5969 cm^{-1} 1I_1 level of the 3F_4 manifold.

Appendix B explains the effects of a long lived lower manifold on the limiting extraction efficiency. With those conclusions, said quantity can be calculated for Tm:YLF as

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Tm:YLF ENERGY LEVELS

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Figure 7

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$$\eta_{ex} = \beta_u / (\beta_u + \beta_L)$$

$$= .171 / (.171 + .049)$$

$$= 78\%$$

This, along with the photon energy decrement from 353.2nm to 452.6nm of 78%, form the major losses of the Tm:YLF systems.

Appendix B also demonstrates how the extraction efficiency raises the saturation fluence. For Tm:YLF on the 452.6nm line, it is

$$E_{SAT} = (h\nu / \beta\sigma) (\beta_u / (\beta_u + \beta_L))$$

$$= 10.7 \text{ J/cm}^2 \quad (\beta\sigma = 3.2 \times 10^{-20} \text{ cm}^2)$$

or

$$E_{SAT} < 34 \text{ J/cm}^2 \quad (\beta\sigma > 9.5 \times 10^{-21} \text{ cm}^2)$$

depending, of course, on which value of $\beta\sigma$ is used.

2.1.4 Fluorescent Lifetimes

Early in the program lifetimes were reported as the time to the 1/e points after the end of the excitation pulse. As the purpose of the system is to store energy, it was realized that the critical parameter is the initial decay rate of the excited ions. It was found that these rates were significantly higher than the long term averages, and respectable losses could occur if this fact was ignored.

When a more comprehensive survey was taken, using crystals and polycrystalline samples of six different concentrations, the data was, therefore, analyzed to yield D_2 initial lifetimes, which are

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the inverse of the initial decay rates. Figure 8 displays the data in this form.

As the fraction of the energy still stored at the end of the pump pulse is

$$f = \frac{T}{\tau} (1 - e^{-T/\tau})$$

where T is the pump pulsewidth (approximated by a 'top hat' pulse" and τ is the initial fluorescence lifetime, 90% storage efficiency is achieved when $\tau/T \geq 5$. Therefore a 5% Tm:YLF crystal can be said to efficiently (i.e. >90%) store a pulse of $T \leq 500\text{nsec}$ and a 3% Tm:YLF crystal efficiently stores pulses of $T \leq 800\text{nsec}$.

2.1.5 Absorption Coefficients

The absorption coefficients of Tm:YLF for XeF radiation were determined both with the Cary 14 Spectrophotometer and by transmission experiments with the Tachisto excimer laser. Figure 9 shows the coincidence between the 351.1nm and 353.2nm XeF output lines and the absorption as measured on the Cary 14. While Tm:YLF shows only small polarization sensitivities, there is a large wavelength dependence: a factor of three to four, depending on polarization. Roughly averaged the coefficients are:

$$\alpha = .055\text{cm}^{-1}/\% \text{Tm at } 353.2\text{nm}$$

and

$$\alpha = .016\text{cm}^{-1}/\% \text{Tm at } 351.1\text{nm}.$$

The active laser absorption measurements were performed by ratioing two energy meters, in front of which a crystal could be placed. The laser was assumed to be completely polarized, by virtue of its two internal Brewster windows and moderate Q cavity. Transmission percentages were converted to average Beer's law coefficients of

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I_{D_2} INITIAL LIFETIME VERSUS CONCENTRATION

FIGURE 8

ABSORPTION SPECTRUM OF Tm:YLF

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Figure 9

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$$\alpha = .038 \text{ cm}^{-1}/\% \text{ Tm}$$

and

$$\alpha = .023 \text{ cm}^{-1}/\% \text{ Tm}$$

This would indicate that the Tachisto's output is somewhat evenly divided between 351 and 353nm outputs. A later experiment with the Optical Multichannel Analyzer showed that this ratio is not constant, a fact which introduces some uncertainty into any measurement of absorbed energy.

2.1.6 Heat Loading Experiment and Modeling

The thermal loading experiment was performed on a sample of 10% Tm:YLF. Figure 10 shows the system schematically. The system was calibrated by substituting a 2.5 x 2.5 x 23mm sample of CS-7-56 Corning Glass for the crystal. It was anticipated that this material would absorb all of the 353nm light and convert it all to heat.

Using the thermistor bridge sensitivity of 12.7mV/°C, and the weight, thermal capacity and true absorption of the glass, the predicted signal was 40.3μV/mJ at 100% conversion to heat. The actual experiment produced only 28.6μV/mJ, or 71% of the prediction.

Using similar data for the 2.5 x 2.5 x 23mm 10% Tm:YLF crystal the predicted heat loading induced voltage rise was 17.3μV per mJ

per percent heat loading. The measured rise of 13.7μV/mJ yielded an unexpectedly high value of 79% heat loading. If one were to correct for the glass sample calibration, the result would be a heat loading value of 118%, obviously false.

A number of factors are thought to have contributed to this result. First, it is possible that the reference sample was bleached by the repeated absorption of the high powered XeF laser beam. To

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Thermal Load Experiment

Thermistor Bridge Circuit

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correct for this, a new reference sample was prepared with five sides (all but the entrance facet) gold plated. This was to ensure that the sample is a better light trap.

If we ignore the calibration run, we are still faced with a 79% heat loading. This has led us to investigate the decay modes of the stored energy. We have defined the three step process that has led to the observed heat loading, and is diagramed in Figure 11.

It is known that in 10% Tm:YLF the 1D_2 lifetime is less than three percent of the lifetime in very lightly doped samples. This means that less than three percent of the decay of the upper level is radiative. Essentially all the ions relax non-radiatively by a resonant process shown as Step 1. This results in two ions in the 3F_4 level and a deposition of 2500cm^{-1} of energy as heat or about 10% of the input energy. Together with the intramanifold relaxation, this results in an 11% heat loading.

In the second step, the two ions in the 3H_4 manifolds are resonantly quenched to the 3F_4 level producing four ions for every one that decayed out of 1D_2 . The intramanifold relaxation produce another 10% heat loading, for a total of 21%.

Finally the ions should decay radiatively out of 3F_4 adding only about 1% to the heat loading. Upon investigation, however, it was found that this particular crystal has an impurity quenched lower level. The measured 3F_4 lifetime of only 5ms corresponds to 67% quenching. This adds 53% to the heat loading for this particular crystal.

Therefore, for this experiment we would now predict a heat loading of 74% very close to the measured 79%.

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TM:YLF ENERGY FLOW

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Figure 11

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Although the value of 74% heat loading is far from that originally predicted for a large Tm:YLF system, the original calculations stand basically unaltered. In the operation of a large system, each of these heat producing steps is mitigated by careful design and fabrication.

Step 1: Since the purpose of the RGH pumped solid state laser is to store energy for a laser pulse, no useful system will have as large a non radiative decay of excited ions as the small scale samples. After depositing 287cm^{-1} (per excited ion) due to the 1D_2 intra-manifold relaxation, about 74% of the excited ions will undergo stimulated emission, producing an ion each in the 3F_4 manifold and an additional 273cm^{-1} heat loading contribution due, again, to intramanifold relaxation. (See Figure 112).

The ions remaining in 1D_2 will decay by resonant transfer, producing another 680cm^{-1} heat contribution.

All totaled, this reduces the Step 1 heat loading from 21% to 4.4% of input energy, which is $28,321\text{cm}^{-1}$ per ion.

Step 2: The effect of concentration on the fluorescence quantum efficiency of the 3H_4 level is not known but it can be estimated that, in a lightly doped, uncontaminated crystal, it should be at least 10%. Combined with the reduced 3H_4 population, the contribution to the heat loading is reduced from 10% to 2.2%, or 640cm^{-1} .

Step 3: The quenching of the 3F_4 level seen in this crystal is quite excessive and atypical. No other boules have shown such a great amount of impurity quenching. It is standard procedure to expect at least 95% fluorescence quantum efficiency of this decay.

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TM:YLF ENERGY FLOW

Figure 12

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With the reduced population of the level, about 1-3/4 ions per excited ion, the Step 3 heat loading should be less than 3.0%; more likely it will be 1% or 183cm^{-1} . All totaled, in a lightly doped crystal under a highly saturating field, the total predicted heat loading is 2063cm^{-1} or 6.5% of the input energy. As the stored energy is

$$E_{ST} = n_{ex} h\nu_{output} = .78 hc/452.6\text{nm} = 17234\text{cm}^{-1}$$

this corresponds to 12% heat loading.

It is unfortunate that this could not, in this program, be demonstrated in the lab. It is not possible to cause lightly doped crystals to lase strongly with the low energy discharge excimer laser currently available. It is likely that a small electron-beam pumped excimer laser would be needed to simulate the conditions of a large system and actually demonstrate the low heat loading that is predicted.

2.1.7 UV Transmission

A sample of 10% Tm:YLF was sent to Acton Research Corp for spectroscopic examination in the near to vacuum ultraviolet. Figure 13 illustrates the onset of the allowed transitions, which is beyond twice the pump photon energy. This is important because any absorption, by excited Tm ions, of either pump or output photons would create significant losses. These would be evidenced by ground state absorption in the 175-180nm and 190-205nm regions respectively. Figure 14 shows an absorption detected at the latter region. While no Tm^{3+} levels should exist at this point we still doublechecked by running both 10% and 1% Tm:YLF crystals in a Cary 14. Figure 15 shows that there was more absorption in the 1% crystal, indicating that we are seeing an impurity absorption, not a Tm state. As only a Tm state can be involved in excited state absorption, this will not be a loss mechanism.

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Box 304 / 525 Main Street / Acton Massachusetts 01720
(617) 263-3584

CALIBRATION CURVE

Customer Sanders Associates
Item Thulium-doped LiYF₄ crystal
End User Evan Chickolis
Type of Test VUV transmission
Date 12/11/78
Comments 10% Tm:LiYF₄
Relative transmission of
4 mm thick. Sample
recorded on McPherson
231 monochromator and
ARC reflectometer

Figure 13

ACTON RESEARCH CORPORATION

Box 304 / 525 Main Street / Acton Massachusetts 01720
(617) 263-3584

CALIBRATION CURVE

Customer Sanders Associates
Item Tin: YLF sample
End User Kevin Chickolis
Type of Test Detail of 1800-2400 Å
Date 1/1/79
Comments ~ 4 mm thick sample
* Relative transmission data.
Data below 2000 Å taken
on McPherson 231, above
2000 Å on GCA EU-700
Spectrometer

Figure-14

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IMPURITY ABSORPTION SPECTRA

OPTICAL DENSITY

Figure 15

2.1.8 Damage Testing

After profiling a sharply ($f/1.5$) focused laser beam with a scanned razor blade, crystals were placed so that the focus was inside them. The maximum available fluences were $490 \pm 100 \text{ J/cm}^2$ or $14 \pm 3 \text{ GW/cm}^2$. Even this fluence did not appear to damage the sample of undoped YLF. It is safe to say that crystals of Tm:YLF can sustain internal fluences of $300 \pm 50 \text{ J/cm}^2$ and $8 \pm 2 \text{ GW/cm}^2$ without damaging, providing the sample is free from inclusions.

2.1.9 YLF Properties

In addition to the UV transmission and damage thresholds, two more important properties of YLF were measured. S. Jacobs and J. Reinherd at the University of Rochester Laser Lab have measured $\Delta n/\Delta T$ in a piece of Sanders undoped YLF at several wavelengths in two polarizations. Table I shows the result. Note that the 442nm σ -polarized value of -8×10^{-7} is quite low, on the order of the best laser glasses. As $\Delta n/\Delta T$ was measured near room temperature only, it was not possible to determine an athermal temperature point.

In a paper in Applied Optics, P. Lin et al⁽¹⁾ were unable to detect any two photon absorption at 266nm. Their system limited upper bound for the two photon absorption coefficient at that wavelength is $\alpha < 4.0 \times 10^{-6} \text{ cm/MW}$.

2.1.10 Sample Growth

During this program a number of Tm:YLF crystals and spectroscopic samples were grown. They included

Boule #554 7cm dia 5% Tm:YLF
Boule #556 7cm dia 5% Tm:YLF
Boule #558 3cm dia 1% Tm:YLF

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TABLE 1

 $\partial n / \partial T$ OF LiYF_4 π polarized σ polarized $\lambda = .064 \mu\text{m}$ $-43 \pm 2 \times 10^{-7} / ^\circ\text{C}$ $-20 \pm 2 \times 10^{-7} / ^\circ\text{C}$ $\lambda = .633 \mu\text{m}$ $-30 \pm 2 \times 10^{-7} / ^\circ\text{C}$ $-16 \pm 2 \times 10^{-7} / ^\circ\text{C}$ $\lambda = .442 \mu\text{m}$ $-30 \pm 2 \times 10^{-7} / ^\circ\text{C}$ $-8 \pm 2.5 \times 10^{-7} / ^\circ\text{C}$

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and spectroscopic, zone refined polychrystalline samples of $\frac{1}{4}\%$, 1%, 5%, 7%, 10% and 15% Tm:YLF.

2.1.11 System Evaluation

The major unknown and largest detractor from the XeF pumped Tm:YLF laser is the efficiency at which the XeF laser can be operated. With the present estimates of 5%, and the theoretical limiting efficiency of the system, due to the change in photon energy, from 351 nm to 453 nm i.e.,

$$\eta = .78$$

and the lower level bottlenecking (See again Appendix A)

$$\eta_{ex} = .78,$$

implying

$$\eta_{max} = .61,$$

the limit of the system is 3% overall.

A number of practical effects, of which the above two are the only fixed ones, limit the conversion efficiency to less than 61%. Each can be dealt with separately, as this is a linear process.

There will be a small loss associated with injecting the pump light into the crystal. This can be made very small, especially compared to a flashlamp pumped system, because of the ease of handling the collimated pump laser output. If dichroics are avoided and the entrance faces properly coated or Brewster angled, this will be a trivial loss.

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Absorbing all the light that does get into the crystal provides a good challenge to the system designer. Absorbing along the system axis (longitudinal) is very efficient and produces good uniformity of the deposited energy, but may need dichroic coatings. Absorbing across the axis (transverse) decreases the stress on the entrance face and eases the requirements on the coatings, but is only practical in systems where the transverse dimensions are on the order of an absorption length. ($3 < L < 30\text{cm}$).

It has already been pointed out that crystals of 3% Tm:YLF can efficiently (90%) store microsecond pump pulses. Fixing the dopant thus fixes the absorption coefficient at $.18\text{cm}^{-1}$ (353nm) or $.05\text{cm}^{-1}$ (351nm). This is a major trade-off as the absorption length can be shortened by increasing the dopant, but only at the expense of storage efficiency. One simple way of mitigating this is to absorb via a multiple pass arrangement which effectively multiplies the absorption coefficient by the number of passes.

As the Nd_2 manifold in Tm is pumped directly, the quantum efficiency of the relaxation to this manifold is unity. In other systems which are pumped via intermediate manifolds which are not in thermal equilibrium with the storage manifold, it is possible for competing mechanisms, such as fluorescence or resonant transfer to decrease this efficiency. In such a system, the time it would take for the excited ions to relax to the upper level will also decrease the storage efficiency. Therefore, non-resonant systems are less desirable than truly resonant ones.

On the issue of operation at high ($\sim 10\text{Hz}$) repetition rates, Table I compares XeF pumped Tm:YLF to a flashpumped glass. As Nd glass lasers generally produce 1.6 - 2.0 J of heat per Joule of stored energy and Tm:YLF produces only 0.12, Tm:YLF has a factor of ~ 15 advantage. Combined with its superior thermal conductivity this

LO gives it a factor of 150 advantage over EV-2 glass.

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TABLE II

THERMAL COMPARISON: FLASHLAMP PUMPED GLASS AND XeF PUMPED Tm:YLF

	EV-2 GLASS	YLF
RELATIVE HEAT LOAD E_H	1	0.07
THERMAL CONDUCTIVITY		
k (W/cm ² K)	0.006	0.06
C_p (J/gm ² K)	0.54	0.79
ρ (g/cm ³ K)	2.7	4
$C_v = \rho C_p$ (J/cm ³ K)	1.46	3.16
FIGURE OF MERIT	0.006	1.2
k/E_H	(1)	(150)
THERMAL DIFFUSIVITY		
$\kappa = \frac{k}{C_v}$ (cm ² /SEC)	0.004	0.019

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2.2 XeF PUMPED Tm:KYF

Doping Tm into KY_3F_{10} has several attractions. Being cubic, there is a potential to hot press forge a crystal, increasing its diameter beyond the size limitation of a given crystal growing furnace. Work has been performed to determine the viability of Tm:YLF in a system similar to that envisioned for Tm:YLF.

2.2.1 Laser Experiments

A laser crystal was fabricated from the best region, determined by visual inspection, of boule #556. Unfortunately it still exhibited a logarithmic loss, due primarily to scatterings, of $\delta_s = .36$ per pass. This would cause a total round trip resonator loss of $\delta = .86$ and require an average gain coefficient of $g = .26$ just to reach threshold.

It is conceivable that this level could be reached with available equipment, but it would involve severely stressing a crystal of visibly poor quality. As it was, the crystal was not selected for fabrication until after several attempts had failed to produce a more promising boule, and the crystal was not ready in time to attempt to lase it on this program.

2.2.2 Stimulated Emission Cross Section

Figure 16 shows the cross section versus wavelength curve for Tm:KYF. At the peak at 449.5nm $\sigma = 9.1 \times 10^{-20} \text{ cm}^2$. As the lower laser manifold is long lived, as in Tm:YLF, the energies of the individual levels are necessary to precisely predict E_{SAT} . Although these have not been specified an estimate can still be made as

$$E_{SAT} \approx 3.7 \pm 1 \text{ J/cm}^2$$

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TM:KYF 1D_2 CROSS SECTION

TM:KYF

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Figure 16

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Therefore, in an operational regime dominated by pulse shape saturation distortion, a Tm:KYF amplifier would require approximately three times the aperture of a similar Tm:YLF amplifier, thus negating the advantage gained by hot forging. On the other hand, systems that can be run with very high fluences without pulse distortion have a large margin between the operating fluence and damage levels.

As KYF is cubic, there is no polarization of the cross section spectra. This allows use of circularly polarized light in those amplifiers employing normal transmission, thus increasing the power handling ability of a system of a given diameter. (42)

2.2.3 Fluorescent Lifetimes

The initial lifetimes of the 3D_2 manifold in Tm:KYF was measured in three polycrystalline and single crystal samples. Figure 17 displays the data in the same form as Figure 8 does for Tm:YLF. Note that the lifetimes are comparable to those of Tm:YLF with the same dopant densities.

2.2.4 Absorption Coefficient

Figure 18 displays the coincidence of the XeF pump lines with the ground state to 3D_2 absorption in Tm:KYF. Note that the absorption coefficients are significantly higher ($.060\text{cm}^{-1}\%$ vs $.030\text{cm}^{-1}\%$) than Tm:YLF. Practically, this means that a Tm:KYF crystal could be substituted for a much more heavily doped Tm:YLF crystal and still retain the same absorption length. The lighter doped Tm:KYF crystal would then have a longer initial lifetime, enhancing the storage efficiency.

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I_{D2} INITIAL LIFETIME VERSUS CONCENTRATION

FIGURE 11.7

COINCIDENCE OF Tm:KYF ABSORPTION WITH XeF LASER LINES

Figure 18

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2.2.5 Known KYF Properties

Being a new material, not as much is known about KYF as about YLF. Its UV edge is not accurately known, because scattering tends to make the crystals opaque in the mid-ultraviolet. A 1% Tm:KYF crystal has exhibited excellent transmission down to 190nm, the limit of the Cary 14. The thermal conductivity was measured, and found to be 0.027 W/cm-sec, about half that of YLF. Its density is about 4.4 g/cm³. Table 3 compares these and other properties of Tm:KYF with those of Tm:YLF.

2.3 XeF PUMPED Nd:YLF

Nd:YLF has many desirable features as a resonantly pumped solid state laser. It exhibits fluorescence in three bands, shown again in Figure 19, around 383nm, 410nm and 447nm. For the 383nm branch, the photon energy efficiency would be 92% and as the lower manifold is thermally quenched, there would be no lower level bottlenecking in pulses of sufficient width. The known defects of Nd:YLF are the inability to dope much more than 1% Nd into a YLF crystal, and its tendency to form a core during growth.

2.3.1 Fluorescence Lifetimes

The initial lifetime of the $^4D_{3/2}$ manifold was measured by observing the 383nm fluorescence, which could not come from another transition (450nm fluorescence could conceivably come from something like $^4G_{9/2}$ to $^4I_{9/2}$ fluorescence). Crystals of 0.5% and 1.3% Nd were tested. Figure 20 shows the results.

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TABLE III

COMPARISON Tm:KYF AND Tm:YLF

PROPERTY

Tm:YLF

Tm:KYF

CRYSTAL STRUCTURE

TETRAGONAL

CUBIC

ABSORPTION $\lambda = 353 \text{ nm}$
5% DOPANT0.30 cm⁻¹0.60 cm⁻¹CROSS SECTION σ_E $3.2 \times 10^{-20} \text{ cm}^2$ $9.1 \times 10^{-20} \text{ cm}^2$

SATURATION FLUX

 10 J/cm^2 $\sim 3 \text{ J/cm}^2$

METASTABLE LIFETIME (5%)

 $2.6 \mu\text{sec}$ $1.6 \mu\text{sec}$

THERMAL CONDUCTIVITY

 0.06 W/cm sec 0.03 W/cm sec

UV CUTOFF

120 nm

 $\leq 190 \text{ nm}$

D BAND ONSET

170 nm

 $< 190 \text{ nm}$

DENSITY

 4.0 g/cm^3 4.4 g/cm^3

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Nd : YLF EMISSION SPECTRUM PUMP 360 NM

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Figure 19

$4D_{3/2}$ INITIAL FLUORESCENT LIFETIME

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2.3.2 Absorption Coefficient

The absorption of XeF radiation by Nd:YLF was measured both with the spectrophotometer and by passing an XeF beam from the TAC II laser through the crystal, in the same manners as Tm:YLF was measured. Figure 21 shows the coincidence with both XeF lines to be about equal. Therefore, it is expected that the absorption would be unaffected by a wavelength shift, such as occurs when XeF is run at high temperatures to attain high efficiency. There is however a strong polarization dependence with π polarized absorption being four times as strong as σ . The laser transmission measurements, corrected again for scattering by a HeNe transmission measurement are,

$$\alpha = 1.02 \text{ cm}^{-1} / \% \text{ Nd } \pi$$

$$\alpha = .50 \text{ cm}^{-1} / \% \text{ Nd } \sigma$$

The three facts above allow a check on the polarization of the laser beam. From this data, the calculated polarization is 80% which agrees well with the general operating characteristics of the TAC II laser.

Oscillator Experiments

Two 4 x 30mm 1% Nd:YLF rods were fabricated and polished. Two attempts were made to lase them.

The first effort involved putting a rod into the Tm:YLF resonator, whose mirrors had enough bandwidth to cover the 447nm transition.

The resonator was aligned by maximizing the output of the Tm:YLF laser. The excimer laser gas was then replenished and the Nd:YLF crystal installed. This was repeated several times, without success. This implies that the stimulated emission cross section is less than

LOW Tm:YLF by, at least, a factor of 2 or that the losses are greater by

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**Defensive
Systems
Division**

Nd:YLF ABSORPTION OF XeF OUTPUT

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FIGURE 21

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at least, about one fourth.

The second attempt involved using a set of mirrors fabricated specifically for the 411nm Nd:YLF transition. This experiment was performed using the more energetic and much higher powered Lumonics 262-2 laser. No lasing was observed, even after several attempts. What was seen, though, was bulk discoloration of the crystal. This appeared to be of the reversible electronic configuration change type that had been observed earlier (See Section 2.6.1). The region of change was very faint and could only be seen by looking directly down the axis of the rod, but it was definitely being caused by the laser beam, as the affected region assumed the shape of the laser beam. A series of these regions was formed as the rod was moved several times. It was not possible to accurately gauge the depth to which these regions extended, but they did appear very shallow on the order of one or two millimeters. As this is much less than the absorption length (10mm π , 20mm σ) this gives evidence for some nonlinear process, such as excited state absorption, which is either very power dependent, giving rise to non-exponential absorption.

Although the transmissison of Nd:YLF has been found to be high, when measured on the Cary 14, down to 200nm, it was not possible for us to determine if the region of transmissivity extended to $\lambda < \frac{1}{2} \lambda_{XeF} = 175\text{nm}$. Available data⁽²⁾ indicates that the cut-off wavelength will be $183 \pm 1\text{nm}$. This would suggest that excited state absorption into the d bands will be a problem.

2.4 OTHER XeF PUMPED SYSTEMS

Most of the other rare earth - YLF combinations were examined in this investigation. They are reported here in order of decreasing atomic number.

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2.4.1 Yb:YLF

Ytterbium YLF has no forbidden transitions below 900nm. The allowed transitions begin around 150nm. It is transparent between these two regions and is therefore of no direct interest.

2.4.2 Er

Erbium YLF is a good laser material in which at least four laser transitions have been demonstrated among the five lowest manifolds. Unfortunately, Er:YLF has no detectable absorption at 351nm or 353nm.

Er:YLF does exhibit ground state absorption into the $^2G_{7/2}$ manifold down to 355nm. If a host were found that shifted the manifold upward by 100-200 cm^{-1} , Er:YLF would be a good XeF candidate although it would involve non-resonantly pumping the $^2G_{7/2}$ manifold. It would probably emit around $\lambda \sim 475\text{nm}$.

2.4.3 Ho:YLF

Holmium YLF is another good laser material in which at least eleven transitions have been lased. Spectroscopically measured absorption coefficients are

$$\alpha = .017 \text{ cm}^{-1}/\% \quad \lambda = 353.2\text{nm} \quad \pi \text{ and } \sigma$$

and

$$\alpha = .006 \text{ cm}^{-1}/\% \quad \lambda = 351.1\text{nm (unpolarized)}$$

Although the second is extremely low (and hence the system is incompatible with efficient high temperature XeF lasers) the first is merely small.

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The expected output of the Ho:YLF would be near 445nm ($^5G_3 - ^5I_7$) or 535nm ($^5G_3 - ^5I_6$). Both of these regions exhibit significant absorption from the ground state. The only way around this difficulty would be to lase around 610nm ($^3G_3 - ^5I_7$) which has a photon energy efficiency of only 58% or try to lase from the non resonantly pumped 5G_4 level at 590nm ($^5G_4 - ^5I_6$) which also has a low photon energy efficiency of 59%.

Given both the incompatibility with a 351nm pump and the low photon energy efficiency, the potential for this system seems much less than Tm:YLF over which it has no obvious advantages. Because of the latter problem is inherent in the wavelength, no mirrors were purchased for the region beyond 500nm. Therefore, no attempt was made to lase Ho:YLF pumped by XeF.

2.4.42. Dy:YLF

Dysprosium:YLF exhibits strong absorption at 351nm. The four coefficients are listed below

α	=	1.22 cm ⁻¹ /%	351.1nm	π
α	=	0.75 cm ⁻¹ /%	351.1nm	σ
α	=	0.12 cm ⁻¹ /%	353.2nm	π
α	=	0.15 cm ⁻¹ /%	353.2nm	σ

Figures 22 and 23 show the absorption curves for 25% Dy:YLF, 6.9mm thick.

If the crystal is being near resonantly pumped, and there exists a long lived level, fluorescence would be expected around 425nm (Level $^6H_{13/2}$) or 470nm (Level $^6H_{11/2}$) or 520nm (Level $^6H_{9/2}$).

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Figure 22
Dy:YLF Absorption, 353 nm Region

Figure 23
Dy:YLF Absorption, 353 nm Region

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An Optical Multichannel Analyzer was set up to try to detect this fluorescence (Figure 24). The only strong fluorescences detected were around 380nm and 480nm. See Figure 25. Some very weak fluorescence was detected at 419nm and 429nm, the latter falling in a ground state absorption band. The 380nm fluorescence appears to be fluorescence to ground state ($^6L \rightarrow ^6H_{15/2}$) and is therefore not useful for our purpose. The 480nm transition has been proposed before. It is, however a $^4F_{9/2} \rightarrow ^6H_{15/2}$ (ground state) transition, which is "three level". $^4F_{9/2} \rightarrow ^6H_{13/2}$ fluorescence would be way down at 580nm. The photon efficiency is down to 60% and the reported cross section is

$$\beta\sigma \sim 5 \times 10^{-21} \text{ cm}^{-2}$$

which is very small.

2.4.5 Tb:YLF

Terbium YLF also exhibits absorption of XeF output. The coefficients are

$$\begin{aligned} \alpha &= .08 \text{ cm}^{-1}/\% \pi \text{ } 351.1\text{nm} \quad \pi \text{ } 353.2\text{nm} \\ \alpha &= .03 \text{ cm}^{-1}/\% \sigma \text{ } 351.1\text{nm} \quad \sigma \text{ } 353.2\text{nm}. \end{aligned}$$

The curves are shown in Figure 26.

The OMA was used to detect fluorescence. Figures 27 and 28 show the strongest fluorescence detected. The wavelengths of the detected bands agrees well with previous work performed on the Tb:YLF system. All emission shown originate on the 5D_3 manifold. The transition to the first excited manifold 7F_5 is the 410nm fluorescence. The calculated cross section for this transition is

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Figure 24
Fluorescence Measurement Using OMA

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(A)

(B)

Figure
Dy:YLF Fluorescence, XeF Pumped

Figure 25
Dy:YLF Fluorescence, XeF Pumped
(A) 382 nm Region
(B) 473-479 nm Region

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Figure 26
Tb:YLF Absorption, 353 nm Region

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Figure

Tb:YLF Fluorescence, XeF* Pumped

Figure 227
(A) 393 nm Region
(B) 409 nm Region

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(A)

(B)

Figure

Tb:YLF Fluorescence, XeF* Pumped

Figure 28

Tb:YLF Fluorescence, XeF* Pumped

(A) 440 nm Region

(B) 453 nm Region

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$$\sigma \sim 3 \pm 3/2 \times 10^{-21} \text{ cm}^2$$

also a very small number. This would correspond to a saturation fluence of

$$E_{\text{SAT}} \sim 150 \text{ J/cm}^2$$

2.4.6 Gd:YLF

Gadolinium:YLF has no transitions below 32000 cm^{-1} and is therefore transparent down to 310 nm , including the region of 350 nm .

2.4.7 Eu:YLF

There is absorption in Eu:YLF at $\lambda > 355 \text{ nm}$, but none at 351 nm or 353 nm . Even if there had been, general spectroscopic transition rates and data from Eu:YAG suggest that these would be weak transition with $\sigma \sim 10^{-21} \text{ cm}^2$.

2.4.8 Sm:YLF

No sample of Sm:YLF was available during this program. A sample of Sm:KY₃FeF₁₀ was made, in the hope that a section of the polycrystalline melt would be clear enough to take absorption measurements on. This did not work, and the sample was awaiting zone refining when the program ended. As there is a weak absorption in Sm:YAG, it is possible that some absorption would be found in Sm:YLF although it probably would not be sufficient.

2.4.9 Pr:YLF

Praseodinium:YLF exhibits no absorption bands between 440 nm and its allowed transition edge, which should be around $170 \pm 20 \text{ nm}$. It

does not absorb XeF laser radiation.

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2.4.10 Ce:YLF

Beyond one line at $\lambda \sim 5 \mu\text{m}$ Cerium:YLF is transparent to $\lambda \sim 300\text{nm}$. It does not absorb XeF laser radiation. Beyond 300nm in YLF, and beyond various other limits in other hosts, are the f-d transitions. Being allowed, they are generally short lived, and are not suitable for this application regardless of pump.

2.5 KrF PUMPED Ho:YLF

Holmium YLF was proposed as a KrF resonantly pumped storage laser. The primary advantage of this system is that it uses the very efficient KrF laser, which is nearly twice as efficient as the XeF laser.

One fluorescent line, almost in the visible, with only a modes lifetime, was found. Evidence suggests excited state absorption occurs strongly.

2.5.1 Absorption

The absorption coefficients at 248.5nm as measured on the Cary 14 are

$$\alpha = .025 \text{ cm}^{-1}/\% \quad \sigma$$

$$\alpha = .016 \text{ cm}^{-1}/\% \quad \pi$$

As the KrF laser is tunable to some degree it is appropriate to determine the highest absorption attainable with less than two nanometers of tuning. Both π and σ Ho:YLF spectra show peaks at $\sim 249.5\text{nm}$ with coefficients

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Figure 29
Ho:YLF Absorption, 248 nm Region

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$$\alpha = .20 \text{ cm}^{-1}/\% \quad \sigma \quad \Delta\lambda = 1.0 \text{ nm}$$

$$\alpha = .10 \text{ cm}^{-1}/\% \quad \pi \quad \Delta\lambda = 0.9 \text{ nm}$$

Absorption measurements were also performed with the TACII laser configured for lasing with KrF. The derived absorption coefficients are

$$\alpha = .40 \text{ cm}^{-1}/\% \quad \pi$$

$$\alpha = .15 \text{ cm}^{-1}/\% \quad \sigma$$

These values are well above the previous ones. A close examination of the original data suggests a power dependency of the result, with the absorption decreasing with decreasing pulse energy (fixed pulsewidth). This may indicate excited state absorption into the d-bands which should begin at $56,400 \text{ cm}^{-1}$, much less than twice $40,000 \text{ cm}^{-1}$ of a KrF pump photon. If this is indeed the case, that excited ions are absorbing pump light and being raised to the 5d regions, it would be a serious problem for most KrF-pumped systems, as only Gd^{3+} has d bands that start above $80,000 \text{ cm}^{-1}$. (3) Fortunately the d-bands are not continuous above their onset, and each ion must be checked individually for transmission at $\frac{1}{2}\lambda_p$ or $\sim 124 \text{ nm}$. As this is close to the band edge of YLF, this is not an easy measurement. The facilities for taking this data are not presently available to us, in any case, and we merely surmise from the disagreement of the absorption measurements that excited state absorption is taking place.

2.5.2 Emission wavelength and lifetimes

Ultra-violet emission lines, including those below the 380nm cutoff of the OMA were searched for with a monochromator and PMT setup illustrated in Figure 30. The monochromator was scanned until fluorescence decay was seen, and then tuned in by maximizing the peak amplitude.

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Figure 30
Fluorescence Lifetime Measurement

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A few lifetimes for fluorescence lines in KrF pumped 2% Ho:YLF were measured and are shown in Figures 31-32. The 310nm line with a lifetime (ignoring the KrF laser pulse in the beginning) of 410nsec only 33ns, shorter than the 400nsec fluorescence back to the ground state, indicates^g that it must be due to some excited state absorption process. The emission was weak but appeared to be fairly broad band.

The 372nm line is the more promising of the two. It lies between two absorption bands, in a relatively clear region of the Ho:YLF absorption spectrum. It's lifetime, of 410nsec is not every suseful. Efficient storage would require pulses of only one to two hundred microseconds. This is probably not enough storage time to justify the method of solid state storage.

2.6 KrF PUMPED Nd:YLF

Nd:YLF was proposed as an alternate KrF pumped storage laser, after Ho:YLF. Its absorption was measured by transmission of an excimer laser beam. Fluorescent lines were detected using the Perkin Elmer E-14 system and lifetimes detected with the monochromator - PMT setup of Figure 30.

While the spectrophotometer detected almost no absorption, the actual laser beam was heavily attenuated. Fluorescence to ground state was only moderately long lived (See Figure 32) and the bulk of the crystal exhibited a major change in appearance from the effects of the laser beam. All in all, Nd:YLF looks totally unexceptable as a KrF pumped candidate.

2.7 KrF PUMPED Tb:YLF AND Tb:KYF

Tb:YLF exhibits absorption in a broad, featureless band around 255nm. This is most likely a weak d-band. Figure 34 shows the spectrophotometric absorption curves. The coefficients are

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(A)

(B)

Figure
KrF* Pumped Fluorescence, 2% Ho:YLF

Figure 31

KrF* Pumped Fluorescence, 2% Ho:YLF

(A) 310 nm (Horiz. Scale: 50 ns/Div)

(B) 372 nm (Horiz. Scale: 100 ns/Div)

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10 DIV

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(A)

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Figure 32
KrF* Pumped, 248 nm Fluorescence

Figure 32

KrF* Pumped, 248 nm Fluorescence

(A) Ho:YLF 2%

(B) Nd:YLF 0.5%

Horizontal Scale: 100 ns/Div

ABSORPTION 248 nm REGION Nd:YLF (UNPOLARIZED)

Figure 34
Tb:YLF Absorption, 248 nm Region

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$$\alpha = .053 \text{ cm}^{-1}/\% \quad \pi \quad 248.5 \text{ nm}$$

$$\alpha = .058 \text{ cm}^{-1}/\% \quad \sigma \quad 248.5 \text{ nm}$$

The coefficients measured with the laser beam transmission experiment are

$$\alpha = .27 \text{ cm}^{-1}/\% \quad \pi$$

$$\alpha = .28 \text{ cm}^{-1}/\% \quad \sigma$$

Again, these are higher, suggesting some deleterious absorption process.

The KrF beam from the TAC II had a startling effect on the Tb:LF crystal. Regions exposed to the beam fluoresced faintly green for several minutes, long enough to be carried from room to room. The activated region fluoresced more brightly than the unaffected regions when illuminated by a mercury penlight. Even low power excitation by the 253nm line of a mercury arc seemed to activate the crystal, as the fluorescence would slowly build over a period of two to four seconds upon first illumination but did not exhibit this behavior on subsequent illumination. This activation seemed to disappear by itself in a matter of hours or days. The laser induced activation was reversed by baking the crystal at 200°C for an hour.

Fluorescence spectra were recorded with the Perkin Elmer E-14 system. The shortest wavelength emission was at 305nm, while the strongest was at 380nm. This is probably 5D_3 to ground state fluorescence ($^5D_3 \rightarrow ^7F_6$). Indeed the next fluorescent band is at 415nm, corresponding to a $^5D_3 \rightarrow ^7F_5$ transition. The 305nm and 325nm bands appear to be another pair, originating on the same line at $\sim 33,000 \text{ cm}^{-1}$ and terminating on the 7F_6 and 7F_5 manifold respectively. Such an upper level would be reached after $\sim 7000 \text{ cm}^{-1}$ of non-radiative decay.

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This would require time which reduces the storage efficiency, and generate at least 10% heat loading by itself.

All these factors considered, Tb:YLF does not appear to be a favorable candidate for KrF pumping.

2.8 OTHER KrF PUMPED SYSTEMS

Going across the Lanthanide series, each ion will be considered in turn.

2.8.1 Yb

The comments on XeF pumping apply here. With no 4f levels, which are necessary for storage, this ion is not useful for KrF pumping. In fact it is transparent at 249nm.

2.8.2 Tm

Tm:YLF exhibits ground state absorption into the 3P_2 manifold down to ~251nm. It is transparent at 249nm. If a host can be found that would shift the position of the manifold by $\sim 500\text{cm}^{-1}$, Tm would be a good candidate for KrF pumped system. The f-f transitions, though, do not in general, vary widely from host to host.

2.8.3 Er

Er:YLF exhibits ground state absorption into the $^4G_{9/2}$ manifold down to ~250nm. It is, though transparent at 248.5nm. A host would be needed that would shift the energy manifolds by $\sim 300\text{cm}^{-1}$.

LaF₃ may be such a host. Unpolarized absorption spectra from the Cary 14 yield a coefficient of $\alpha = 1.0\text{ cm}^{-1}/\%$.

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Active laser measurements yield values of

$$1.8 < \lambda < 2.2 \text{ cm}^{-1}/\%$$

depending on polarization. The crystal quality is not known, but some scattering is evident. Therefore this is an encouraging result. Questions remain, though on the suitability of the biaxial LaF_3 host.

2.8.4 Dy

Figure 35 shows the ground state absorption of Dy:YLF at room temperature. 248.5nm is deep within one of the few clear spectral gaps. Even if the laser were tuned toward 250nm or a host found to shift the levels upward, there are no large energy gaps to cause the ion population to build up. Also, at $\lambda \approx 490\text{nm}$ Dy is a jungle of ground state absorption lines with very few clear spectral regions, primarily 305-320nm, 405-425nm and 435-445nm.

2.8.5 Gd

No samples of Gd:YLF were available. There is some indication that it would absorb into the $6^1_{1/2}$ manifold or $6^3_{9/2}$ manifold, but its lack of lower excited states, and its singlet ground state diminish the possibility of making an efficient storage laser out of Gd.

2.8.6 Eu

Eu:YLF exhibits weak absorption down to 250nm, but is transparent at 248.5. The same comments about shifting the energy levels apply here as in Er.

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**Defensive
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ABSORPTION, 248 nm REGION Dy:YLF (π)

72

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2.8.7 Sm

No samples with trivalent Sm were available during this program. No Sm:YLF has ever been grown, although it is certainly possible to do so. The standard references do not extend to this region, and no judgement can be made at this time.

2.8.8 Pr

Pr has one 4f level above $23,000\text{cm}^{-1}$ but it is at $\sim 50,000\text{cm}^{-1}$ nowhere near 249nm.

2.8.9 Ce

Ce:YLF absorbs beyond 300nm into the 5d bands. This has been used⁽⁴⁾ to make a tunable UV laser from 308-325nm. The short (nsec) lifetime of the upper laser level makes it unsuitable for this application.

2.9 XeCl PUMPED SYSTEMS

None of the rare earth ions examined absorb at 308nm when doped into YLF. Data from a small sample fabricated and measured at MIT several years ago indicate that 308nm may lie in the transparent region between the $6P_{5/2}$ and $6P_{7/2}$ manifolds of Gd:YLF. No Sm^{3+} sample was available.

2.10 FLUORESCER SYSTEMS

Frequent reports of 50% fluorescence efficiencies of E-beam pumped RGH. fluorescers have prompted examination of fluorescence pumped systems. While such systems lack the manageable optical coupling and narrow spectral width of laser pumped system, the

Low increase in pump efficiency may be more than compensating.

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Figure 36 shows such a system involving an XeBr fluorescer and Tm:YLF. Such a system is, essentially, a narrowband flash lamp pumped system. It was beyond our capabilities to experiment with this concept, as building a fluorescer would probably involve modifying an e-beam pumped RGH laser.

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FIGURE 36
Tm:YLF - XeBr* SPECTRA

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3.0 MATERIALS

3.1 CRYSTAL GROWTH OF FLUORIDE MATERIALS

Sanders crystal growth facility has been involved with the development of crystalline fluoride materials, with emphasis on the laser host LiYF_4 (YLF), for over 10 years. The crystal growth facility centers around the automated control furnace (Figure 37) in which crystal growth experiments for this program were carried out. The existing hot zone was designed to grow 30mm YLF crystals. Monitor and control of the growing crystal is performed by a unique electro-optical system in which a laser beam is employed to "observe" the growth and produce an input signal for the computerized controller. This system provides a continuously looping control.

The furnace consists of stainless steel high vacuum construction to minimize contamination from the furnace walls. The hot zone consists of a graphite resistance heater enclosed in a series of insulating molybdenum heat shields. A high purity atmosphere is created by pumping the system to a vacuum of less than 30 μPa and backfilling with high purity argon to a pressure of 140 kPa.

The melt is typically processed in Sanders' hydrofluorination system prior to entering the crystal growth furnace. The hydrofluorination system consists of a platinum lined ceramic tube, sealed at each end with Teflon caps, situated in a Kanthal coil heated furnace. The feed is usually purchased as either the oxide or carbonate powder and converted to the fluoride at a temperature below the melting point, using flowing HF. The converted fluoride powder is then melted under flowing HF in the cycle to complete conversion and reduce the surface area and volume.

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CRYSTAL GROWTH SYSTEM

FIGURE 37

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3.2 SIZE SCALING OF CRYSTAL GROWTH OF RE:YLF

3.2.1 Summary

The scaling in fabrication of large crystalline fluoride apertures is a significant development for the Advanced Laser programs. Crystalline fluorides, as a class, display certain generalized properties - such as low n_2 and high ultraviolet transmission - which are desirable for many laser applications. In addition to the application of this materials technology to solid state storage lasers, scale of the growth of this class of materials has application to other aspects of high power laser technology, namely:

- a. Nd:YLF has been identified as the most promising oscillator material for phosphate⁽⁵⁾ and fluoroberyllate⁽⁶⁾ systems;
- b. $\text{KTb}_3\text{F}_{10}$ and LiTbF_4 have the highest figures of merit for faraday rotator materials;⁽⁷⁾
- c. Recent measurement⁽¹⁾ of the two photon absorption coefficient of YLF in the ultraviolet indicate that YLF is a candidate window material for high power RGH lasers and appears to be an excellent candidate uv coating material⁽⁸⁾.
- d. KrF pumped Ce^{3+} :YLF has been lased⁽⁴⁾ and provides a tunable coherent ultraviolet source (This is a non-storage laser).

The growth scaling experiments resulted in growth of 100mm diameter single crystals of Er:YLF. The first 100mm crystal is illustrated in Figure 38 taken during the growth process. The experimental approach taken consisted of a two-step scaling program. The initial scaling experiment produced two 65mm diameter crystals of Tm:YLF. Modifications were made in the hot zone assembly, seed

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100mm DIAMETER CRYSTAL OF Er:YLF DURING GROWTH

FIGURE 38

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rod and seed puller, and growth parameters based on observations and measurements made during this experiment. These modifications were employed in the second series of experiments which were successful in scaling growth of Er:YLF crystals to 100mm diameters.

3.2.2 Growth Scale of 65mm Diameter YLF Crystals

3.2.2.1 Hot Zone Design

The large crucible for growth of 70mm boules and hot zone purchased under Contract ES-77-C-02-4308:A000 was installed and evaluated (Figure 39.) A test growth run was performed to evaluate the thermal distribution of the hot zone. The crucible was positioned in the upper level of the hot zone to optimize the thermal distribution. The test run indicated an adequate thermal balance was achieved and no further modification was necessary.

3.2.2.2 Growth Parameters

Physical growth parameters used in growth runs 554 and 555 were similar to growth runs of pure LiYF_4 . Pull rates, governing the rate of growth, were set to 1.5mm/hr. Seed rod rotation rates of 6rpm were employed for growth runs 554 and 555 to maintain a stable crystal-melt interface. Figure 40 illustrates the effect of certain physical parameters on the crystal interfacial shape and circulation of the melt. Boules 554 and 555 display a saucer-shaped interface. This condition is not advantageous for maintaining a homogeneous melt composition, as the liquid flow is uneven and mixing incomplete. The rotation rates in later growth runs of large boules were increased to develop a flat interface to maintain an even mixing throughout the melt.

The composition of the boules grown were $\text{LiY}_{.95}\text{Tm}_{.05}\text{F}_4$. The chemical nature and size of the thulium ion is similar to that of

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FIGURE 39

Hot zone for crystal growth
of 70mm fluoride crystals

EFFECT OF GROWTH PARAMETERS ON INTERFACE SHAPE AND CIRCULATION IN MELT

Figure 40

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yttrium and therefore is accommodated easily into the tetragonal structure of YLF as a direct replacement for yttrium. Tm:YLF is similar to pure YLF and melts incongruently. As such, the melt was prepared rich in LiF.

3.2.2.3 Results of Crystal Growth

Tm:YLF, Boule 554, was fabricated in the initial growth run for the scaling experiment, Figure 41. The boule was grown to a 60mm diameter and 30mm length. Initial examination of the boule with a HeNe laser indicated material of excellent optical quality. The furnace parameters employed for growth of large diameter crystals were evaluated by the early termination of the run and examination of the boule.

Growth size was expanded to 65mm with the crystal growth of Boule 555, Figure 42. Similar parameters were employed, developed from the previous run to grow to an overall length of 100mm. Boule 555 consisted of 1.2 kilograms of fluoride material. The material from the upper and middle section of this boule was of high optical quality as determined from initial examination with a HeNe laser. The lower section developed a circumferential crack upon cooling. It was suspected that the initial cooling rate was too large for this mass and the crack was the result of thermal shock induced stress.

3.2.3. Crystal Growth of 100mm Diameter Fluoride Crystals

3.2.3.1 Hot Zone Design

The design and fabrication of the enlarged hot zone for growth of large fluoride crystals was completed early in the program. The assembly was modified to a degree based on observations made during the initial scaling experiments. These modifications included raising the crucible position in the hot zone and enlarging the opening in the top horizontal heat shield to alter melt flow patterns

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FIGURE 41

Figure 42

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to generate complete mixing at the crystal-melt interface. The hot zone assembly is represented by the schematic in Figure 43. The following items were fabricated:

- ① Heating element (high purity graphite)
- ① Radiation shields (molybdenum)
- ① Crucible (platinum)
- ① Crucible support cup (high purity graphite)
- ① Crucible support spider (high purity graphite)
- ① Crucible lift rod (high strength graphite)

The crucible has a diameter of 203mm at its mid-height. Literature reports of investigations of maximum crystal diameter/crucible diameter ratio suggests that a value of .5 to .6 is suitable for both silicon⁽⁹⁾ and gadolinium gallium garnet (GGG)⁽¹⁰⁾ to maintain favorable circulation in the melt to prevent impurity segregation which may lead to defect formation in the crystal.

Various studies^(11, 12, 13) have shown that the growth of larger diameter crystals involves a condition where the melt/solid interface changes from a convex configuration with the melt to a flat interface, termed the "flip" diameter. The condition is generated in part because the hydrodynamic shear at the interface causes the centripetal forces generated by the natural convection in the melt to be overcome by the centrifugal forces generated by the rotating crystal. The interface thus becomes a "pump" causing two circularly symmetric flow patterns to develop, one immediately below the interface, the other associated with convective forces in the melt.

Experience with the growth of Nd:YLF suggested that the pre-flip circulation is more desirable, and was retained for that compound by reducing the rotation rate. Unfortunately, the experiments were not complete enough to determine whether the pre-flip circulation is mandatory for the growth of YLF.

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FURNACE ARRANGEMENT FOR 100mm FLUORIDE CRYSTALS

Figure 43

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It is expected that interface transition will occur upon growth of large diameter boules unless the appropriate parameters can be altered without hindering the process; i.e., increase thermal gradient, or reduce boule rotation rate. Transition to a flat interface rather than the intermediate case will be advantageous to maintain proper melt mixing. The liquid mixing for the intermediate case "saucer" shaped interface is not continuous about the crystal interface and may cause crystalline defects due to impurity segregation.

3.2.3.2 Seed Rods Assembly

Modification of the seed rod design and fabrication of the new seed rod was completed. The new seed rod was designed with the growth of large crystals in mind. The new design increased the stability of the growth process by eliminating mechanical vibrations translated to the melt. The stiffness of the seed rod was increased by the following:

- The alloy used was annealed 17-7 pH s.s. rather than 304 s.s.
- The seed rod diameter was increased to 3/4 inch from 5/8 inch of the old design.

Installation of the assembly onto the crystal furnace was completed early in this program.

Further details of scaling issues have been addressed for TSS growth of 100mm to 200mm boules. In particular, the design of the seed holder was altered. The previous design called for the seed to be attached to the molybdenum seed button with platinum wire. Problems with stretching and breaking of this wire had occurred in the growth of 60mm diameter boules. The new design is illustrated in Figure 2445. The "finger" of the seed holder will mechanically support the seed and growing boule, thus eliminating the platinum

wire link. The seed size used for growth of 100mm crystals was

10mm square.

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SEED HOLDER FOR GROWTH OF 100MM FLUORIDE CRYSTALS

Figure 44

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3.2.3.3 Growth Parameters

As discussed earlier, relevant growth parameters include seed rod rotation rate, crystal diameter, furnace thermal gradient, and seed pull rate. The seed pull rate was maintained at 1.5mm/hr. Rotation rate of the seed rod was increased for this growth run from 6 to 10 rpm. It was observed that the crystals grown during the initial scaling experiments displayed a "saucer shaped" interface. Increasing the rotation rate, all other things being equal, will drive the crystal interface to a "flat" configuration. A crystal growing with this type of interface will have less tendency for defect incorporation due to impurity segregation in the melt.

3.2.3.4 Results of 100mm Diameter Crystal Growth Experiments

Two boules of Er:YLF, nominal diameter of 100mm were grown.

During the initial growth attempts, boule 563a was grown. This boule was photographed during the growth process, Figure 45. The photograph was taken shortly after diameter control was initiated. Further on into the growth run a spring failure in the seed rod cooling gland created excessive vibration in the seed rod, which

when translated to the melt, caused the seed to fracture at the seed-holder interface, and loss of the boule into the melt. No evaluation on the quality of the boule was possible prior to the melt-back.

Boule #563b was grown during the next series of attempts. This boule is illustrated in Figure 46. The diameter of boule #563b was maintained just under 100mm and grown to a total length of 60mm. Straight wall length of about 15mm was obtained.

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100mm DIAMETER CRYSTAL OF Er:YLF DURING GROWTH

Figure 45

Figure 46

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Growth rate was maintained at 1.5mm/hr. The rate of diameter outward movement was 3-5mm/hr. This rate of diameter growth was slowed considerably from previous crystal growth runs of large crystals. As the growth parameters were developed, a large thermal lag in the melt was observed, which was not considered at the beginning of growth run 563a. As a result diameter growth rate averaged about 15-20mm/hr for boules 536a, whereas the rate was 3-5mm/hr for boules 563b. It is generally desirable to maintain a slower rate of diameter enlargement to prevent defect formation caused by rapid growth in the radial direction. Boule 563b was pulled to develop about 15mm of straight wall growth and terminated to evaluate growth parameters.

Boule #563b grew with a concave interface. The increased rotation rate of the seed rod, coupled with the significantly larger boules diameter, may have created too much centrifugal force altering the melt thermal gradient such that the center of the crystal melted. Minor changes in the hot zone may have decreased the radial thermal gradient. Less severe gradients will reduce the centripetal forces generated by natural convection in the melt and make the forces created by the pumping action of the boules more dominate upon the melt circulation at either a smaller diameter or lower angular velocity. The machined seed holder displaced the seed .75 inch from the water cooled seed rod. It was observed, from melt back conditions, that the seed holder acted as a sink and reduced the cooling of the seed. Some correction for this affect was accomplished by raising the crucible to a higher level and thus removed the seed holder from the hot zone. Further evaluation to fine tune the hot zone and growth parameters for growth of large boules will be required.

3.2.44 Discussion

The growth of 100mm crystals has demonstrated the size scaling ability of Sanders' technology to expand the process and fabricate large crystals of YLF. The potential laser aperture has more than

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increased by a factor of three during the present program. Figure 47 illustrates three boules of Re:YLF grown for this program. Future scaling experiments to reach the goal of 40 cm apertures will proceed in two defined directions. The first method will employ the present technology of TSS crystal growth and expand furnace capacity; the second method will evaluate and develop a new growth method, bottom seeded solution (BSS) growth.

Expanding the TSS growth technique will require a larger vacuum chamber. This new system would be a scaled version of the existing system. Further scaling issues, including seed rod mechanism, hot zone, and growth parameters, should be straight-forward as all these issues have been demonstrated as scalable during this program.

Bottom seed solution (BSS) growth has substantial potential for growth of very large single crystals of the fluorides of interest for high power laser fusion. A major point is the economics involved in the scaling of growth. Top-seeded solution (TSS) growth requires a furnace hot zone to accommodate a crucible at least twice the diameter of the growing crystal; whereas in BSS growth, the crystal actually extends to the crucible wall. For the same size crucible, a BSS grown crystal will be, at a minimum, twice the diameter of the TSS crystal. In contrast to TSS growth, the crystal would be supported by the crucible that contains the melt rather than the smaller cross-section of the seed at the end of a rotating shaft. For growth of very large crystals, e.g., for crystals 20cm diameter, this change of support can be important, especially if the desired crystal has poor mechanical properties, such as low strength and cleavage.

BSS growth based on the Schmid-Viechnicki technique⁽¹⁴⁾ may be applied to the growth of large YLF crystals. The major difference, sapphire melts congruently and YLF melts incongruently, in BSS

CRYSTALLINE BOULES OF RARE EARTH DOPED LiYF_4

Figure 47

growth is that the melt will change in composition as the crystal grows. Figure 48 displays a possible furnace assembly for BSS BSS growth. The seed is located in a recess at the bottom of the crucible. The seed is cooled by a heat exchanger entering through the furnace bottom; the heat exchange media being either gas or liquid. The thermal gradient in BSS growth, unlike TSS, is developed with the center of the bottom of the crucible the coldest. The melt is contained in the remainder of the crucible above the seed. The crucible-heat exchanger assembly is supported by a refractory structure, such as graphite, which in turn is surrounded by the heating element.

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Figure 48
POSSIBLE FURNACE ASSEMBLY FOR BSS

3.3 CRYSTAL GROWTH OF KYF

3.3.1 Introduction

KY_3F_{10} is of interest as a laser host because the isotropic nature of the material presents the potential of hot forging for diameter enlargement. The crystalline structure of KYF is a modified fluorite structure consisting of potassium ions at the corners, yttrium at the face centers, and fluorine occupying two distinct positions within the unit cell.⁽¹⁵⁾ KYF has been described as a congruently melting compound displaying no sub-solidus transformation.⁽¹⁶⁾ Recent evidence indicates, however, a limited range of solid solution in compositions over 25 mole % KF exists.⁽¹⁷⁾ Sub-solidus transformations may also occur. Similar to other crystalline fluorides, KYF displays low values of n and n_2 , 1.49 and 6×10^{-14} ESU,⁽¹⁸⁾ respectively. As exhibited by YLF and other large band gap fluorides, KYF should be transparent well into the UV. These optical properties are ideal for a laser host and window material.

Limited growth development has been performed on KYF prior to this investigation. Results of two previous growth attempts are known. Airtron has investigated growth of KYF employing an active atmosphere, H.F. Crystals grown displayed a hazy appearance.⁽¹⁹⁾ M.I.T., employing inert argon also grew crystals containing what appeared to be a second phase. The scatter centers appeared inconsistently in the crystals and were related to oxygen contamination. Sections of very clear material were obtained from these crystals. As a result of inconsistent data concerning growth of KYF, further investigation was warranted.

The process development for fabrication of new materials such as KYF require extensive investigation involving raw material selection and initial processing, process atmosphere, and feed composition, as well as growth thermal gradient and other growth parameters. These

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separate variables should be concentrated upon individually to optimize the total process. This was carried out through growth experiments. Initial growth runs and growth parameter development were performed in Sanders' experimental fluoride growth system (Figure 49). The manually operated furnace is a scaled down version of the automated growth furnace, without the computer automated control. Manual operation and control by a highly qualified technician has been advantageous in the early stages of growth development to optimize growth parameters. The hot zone allows growth of boules 25mm in diameter. High purity argon atmospheres, $O_2 < < 1$ ppm, are obtained with the titanium getter system purchased on this present contract. The raw materials, oxides and carbonates, were converted to fluorides in a platinum-lined reactor.

3.3.2 Material Preparation for Crystal Growth

3.3.2.1 Powders

The powders processed for feed were carefully chosen to avoid contamination due to handling. As such, the yttrium oxide and potassium carbonate employed were of the highest purity materials commercially available. Y_2O_3 , purchased from Research Chemicals, contained at the most 10ppm rare earth ion impurities. Concentration of alkali and alkaline earth ions which are not known, however, may be relevant.

Ultrax grade K_2CO_3 was supplied by J. T. Baker Company. The chemical analysis of the K_2CO_3 is listed in Table 4.

Yttrium oxide was converted to yttrium fluoride in the hydro-fluorination system prior to mixing with K_2CO_3 . The conversion rate was initially monitored by weight change of the material. Later, a time-temperature cycle was developed. YF_3 and K_2CO_3 were mixed in specific ratios and processed for the final fluoride conversion. KF was not added directly as this material displays deliquescent tendencies.

Figure 49

EXPERIMENTAL FLUORIDE CRYSTAL GROWTH SYSTEM

TABLE 4

POTASSIUM CARBONATE, ULTREX
For Application in Fiber Optics Manufacture

COMMODITY NO. 5157	
LOT NUMBER: 512561	
DATE OF ANALYSIS: 5/2/75	
DATE PACKAGED: 8/14/78	
FORMULA: K_2CO_3	
FW: 138.21	
	<u>ACTUAL ANALYSIS</u>
ASSAY (K_2CO_3) (by acid-base titration, after drying at 285°C for 4 hours)	100.00 % ^a
Loss on drying at 285°C for 4 hours	0.40 %
Particulate matter (after solution in water)	0.001%
NON-METALLIC IMPURITIES	
In parts per million (ppm)	
ARSENIC (As) ^b	0.04
HALIDES (as Cl)	3
Nitrogen Compounds (as N)	6
Phosphate (PO_4)	3
Sulfur Compounds (as SO_4) ^c	1
TRANSITION ELEMENTS ^d	
In parts per million (ppm)	
CHROMIUM (Cr)	0.01
COBALT (Co)	0.01
COPPER (Cu)	0.01
IRON	0.1
MANEANESE (Mn) ^e	0.02
NICKEL (Ni)	0.02
VANADIUM (V)	0.01

a - Based on 3 determinations: 99.99%, 99.99%, and 100.02%

b - By evolution and silver diethyldithiocarbamate photometry.

c - By barium sulfate turbidimetry in methanol-water.

d - Average values for duplicate samples analyzed by dc-arc spectrography (after collection via coprecipitation with indium using 8-quinolinol-tannic acid-thionalide and ignition to oxides against commercial standards in indium oxide, reading of lines in 2450-3875 Å region); key elements found at or below a significant blank value are reported as < (equal to or less than) one-third of the blank, key elements found at or below a blank near the detection limit are reported as < (less than) the detection limit, the blank values found have been deducted in all of the reported values.

e - By atomic absorption spectrophotometry.

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3.3.2.2 Atmosphere

Hydrogen fluoride supplied by Matheson gas at a minimum purity of 99.9% was used in Sander's fluorination system. Titanium gettered argon was used to flush the fluorination system at the beginning and at the end of each cycle. Welding grade argon, typically containing 10ppm oxygen was purchased and scrubbed in a titanium getter to reduce the measured oxygen concentration to a maximum of 1ppm. The titanium getter system was improved later in the program, under contract with the Department of Energy, and decreased the oxygen contamination level to much less than 1ppm.

The argon used in the Sanders's fluoride furnace in this portion of this program was supplied by Airco. The impurity level was less than 1ppm. The oxygen content of the furnace atmosphere was monitored by an oxygen sensor.

3.3.3 Crystal Growth of KYF

The pertinent parameters variations and results for growth of KYF are summarized in Table 5. During the early growth runs furnace thermal distributing and growth rates were examined to determine the growth characteristics of KYF. This cubic fluoride, unlike $K\text{TaF}_6$ does not display high emissivity. As a result thermal distribution was adequate and the furnace did not require modification. The grown crystals did display scatter centers, which are related to a second phase precipitate. Later growth runs investigated the cause and prevention of these scatter centers.

Growth Run 1

At the beginning of this program KYF seed material was not available. The purpose of the initial growth run was to grow material for seed fabrication. Growth rates in the order of 4mm/hr were used based on previous experimental work. The feed composition was batched

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Table 5
SUMMARY OF CRYSTAL GROWTH OF KY_3F_{10}

<u>G.R.</u>	<u>CRYSTAL NO.</u>	<u>COMPOSITION</u>	<u>GROWTH PARAMETERS</u>	<u>FEED COMPOSITION</u>	<u>EXPERIMENT</u>	<u>RESULTS</u>
1.	556	$KY_{2.85}Tm_{.15}F_{10}$	4.5mm/hr 30rpm	.5% Excess KF	Grow seed material Seeded on molybdenum wire	Material contained uniform haze, composed of twin crystals. Seed mat'l fabricated in 100 orientation laser sample fabricated
2	557	$KY_{2.85}Tm_{.15}F_{10}$	3.0mm/hr 60rpm	Residual from 556 KF rich	Evaluate hot zone & growth parameters	Severe thermal gradient developed driving crystal interface deep into the melt. Rotation of crystal increased to compensate. The crystal was cloudy, related to either too rapid growth rate, excess KF in melt, or impurity.
3	560	$KY_{2.95}Tm_{.05}F_{10}$	1.5mm/hr 30rpm	.5% Excess KF	Evaluate growth rate dependence	The crystal grew with a smooth surface, but cloudy matrix. The scatter appears to be related to a second phase. The scatter is concentrated in lower sections; growth rate not a factor.
4	561	$KY_{2.85}Tm_{.15}F_{10}$	1.5mm/hr 30rpm	.5% Excess KF	Hydrofluorinating system evaluated for contamination (oxygen)	The crystal grown from material processed during the test was cloudy. A leak was discovered in the seed rod, possibly contaminating the melt.
5	562	$KY_{2.85}Tm_{.15}F_{10}$	1.5mm/hr 30rpm	.5% Excess KF	Reevaluated H.F. Process	The crystal was cloudy, indicating that oxygen contamination during the H.F. process was not a problem.
6	567	$KY_{3.0}F_{10}$	1.5mm/hr 10rpm	Stoichiometric	Growth in large furnace O_2 monitored	The crystal was grown from melt in platinum crucible, oxygen maintained < 1ppm. The crystal displayed a frosted surface. A multitude of twin grains developed. Precipitate was observed parallel to twin grains and very dense in the lower section of the boule. Clear samples 10mm x 10mm x 5mm were obtained from the top of the crystal.
7	569	KY_3F_{10}	1.5mm/hr 10rpm	1.0% Excess YF_3	YF_3 rich melt - to observe crystal- lization path.	Crystal was cloudy, excess YF_3 in melt did not affect growth.

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slightly potassium rich to maintain melt composition close to stoichiometric. Figure 50 displays boule 556 grown during this run.

This crystal was seeded on a molybdenum wire and weighed 83.2 gm.

Microscopic examination indicated that the crystal was composed of four twin crystals. Individual crystals were orientated to fabricate seeds to grow in the (100) direction. The material also displayed a "hazy" appearance. The crystal was uniform in respect to the optical scatter. This phenomenon was initially related to a rapid growth rate.

Growth Run II

The prime objective of this growth run was to optimize the thermal distribution, thermal shielding, for growth of KYF. It was confirmed that KYF, unlike KTb_3F_{10} , does not display significant radiation loss resulting in unfavorable uniformity of the thermal distribution. On the contrary, it was observed that severe thermal gradients developed causing the crystal interface to grow very deep into the melt resulting in the loss of a crystal during growth. The melt circulation was increased to reduce the thermal gradient by increasing crystal rotation from 30 to 60rpm. Upon completion of the growth run, modification was made to the radiation shielding to reduce the thermal gradient.

Boule #557, Figure 51, was grown at a rate of 3.0mm/hr. The feed was from the same batch processed for the initial growth experiment. This crystal appeared very hazy, the lower section was opaque. The scatter density of boule #557 was significantly higher than in Boule #556. The possible causes that could result in the creation of scatter centers include: too rapid a growth rate, impurity precipitation, precipitation of an intrinsic second phase. The composition of the melt for growth #557 was considerably richer in KF as a result of drawing the crystal from the earlier growth.

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FIGURE 50

Boule #557
5% Tm:KY₃F₁₀

FIGURE 51

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Growth Run III

The effect of growth rate was examined during Growth Run III. Growth rate was reduced to 1.5mm/hr, one-half the earlier value. Boule #560, Figure 52, was grown during this experiment. The crystal weighed 105gm.

Lower growth rate did not reduce the scatter in the material. The scatter centers seem to be related to a second phase precipitate in the matrix of KYF. Similar to boule #557, the density of scatter sites in boule #560 increased as the crystal was pulled from the melt. The top of the crystal was relatively clear; whereas the bottom was opaque.

Growth Run IV

The next growth experiment examined the possibility of feed contamination during processing. The hydrofluorination reactor was tested for possible leaks during the process. Similar growth parameters were employed as in the previous run, pull rate - 1.5mm/hr, and rotation rate 30rpm. Boule #561 was grown during this run, Figure 53, weighing 145gm.

Upon examination of boule #561, it was determined that this material contained a large concentration of scatter sites. Feed contamination during processing did not seem to be a factor. A leak in the cooling circuit of the seed rod was discovered upon completion of the test which leaves these results inconclusive as introduction of water would result in oxygen contamination of the melt.

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FIGURE 52

FIGURE 53

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GROWTH RUN V

Growth experiment IV, to examine possible contamination mechanism during feed preparation, was run again. Due to the furnace leak discovered, results of growth run IV were disregarded. The furnace was repaired and leak tested thoroughly prior to this test. The same growth parameters were employed for this growth run as used in the previous runs. The results of the growth, boule 562, indicated there was still a problem in the process as the matrix contained the cloudy precipitate. Figure 54 exhibits boule #562.

Growth Run VI

Growth run V was performed in the automated growth furnace. Growth data and results from previous runs could be compared to results in a separate furnace. Contamination due to furnace leaks was eliminated. The furnace atmosphere was circulated and the oxygen potential measured. Oxygen impurity levels were well below the 1ppm level. The melt composition was altered to grow from a stoichiometric batch, 25 mole % KF, 75 mole % YF_3 . Growth from a stoichiometric composition will eliminate the possibility of a sub-solidus precipitation reaction similar to that observed in KTb_3F_{10} grown from KF rich melts. Contamination of the melt during processing was prevented by detailed leak testing of the hydrofluorinating reactor and crystal furnace components.

The observed precipitate was not affected by the modification of the parameters discussed. Boule #567 is displayed in Figure 55. The upper section of the crystal was clear, the precipitate concentration slowly increased, the bottom of the crystal was opaque. The crystal appeared to contain a series of twin boundaries, at which the precipitated phase concentrated. The characteristic was not noted in earlier samples. A clear section 10mm x 10mm x 7 mm was cut and polished to be used to measure the u.v. edge of KYF.

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FIGURE 54

Fig 55
FIGURE 55

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Growth Run VII

The crystallization path was again the main interest in the growth experiment. Feed prepared with excess YF_3 was used for this experiment. Boule #569 was pulled during this growth run, Figure 56. Again the matrix of the crystal contained the precipitate. The high concentration of twinning and preferential segregation of precipitates to these areas was again noted, similar to Growth Run VI.

3.3.4 Zone Refining of KY_3F_{10}

Zone refining experiments were performed to identify to a greater detail the crystallization characteristics of KYF. Specifically, the phase content of the charge and the solid state reactions was observed.

A 500 g charge of KY_3F_{10} melted in HF at Sanders was zone refined in cm 18" long vitreous carbon boat. The experiments confirm that KY_3F_{10} is congruently melting. Even after extensive processing, traces of a second phase remained in the charge. Other work at MIT has indicated that the vitreous carbon boat may contribute impurities to the charge. Zone refining was continued in a 20" long Pt boat and there appears to have been an improvement in the quality of the purified material. Further experiments will be needed to observe the degree of purity obtained with this process.

Physical Properties of KYF

Samples of KYF grown for this project were sent to the Laboratory of Laser Energetics, University of Rochester, and the Material Science Center, Honeywell Corporation. The properties to be measured at the University of Rochester include refractive index, physical density, α_n/α_t , thermal conductivity, thermal expansion. Samples on Table XX list the properties that have been requested. Samples sent to Honeywell will be used to perform forging experiments.

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3.3.5 Discussion of Results

Samples of clean, homogeneous single crystal KYF have been fabricated from boules grown during this program. Two related mechanisms have been observed, which has resulted in low yield from growth runs. These mechanisms, namely scatter centers and cleavage, have appeared consistently in KYF crystals and have concentrated in the lower sections of these crystals. The work in the later portion of the program has concentrated on determining the nature of these defects through growth experiments, and zone refining experiments. The scatter centers seem to be a second phase that has precipitated during the cooling cycles. The precipitation tends to proceed in particular crystallographic directions, $\langle 111 \rangle$. KYF displays octahedral cleavage, which causes cracking in the $\langle 111 \rangle$ directions. The formation of a precipitated phase is seen as aggravating the cleavage tendency as the result of induced stress in specific crystallographic planes.

Variations in growth parameters were made to alter growth conditions in search of causes for the formation of scatter centers. Among the variations investigated, the following were included; growth parameters, feed processing cycles, and the hardware in which KYF was processed and ultimately formed into single crystals. The following conclusions can be made related to the formation of scatter sites as a result of this study:

- The scatter centers in the crystals are related to a second phase precipitate
- The precipitate tends to segregate in particular crystallographic directions (111), and especially along twin boundaries
- The precipitate formation seems to create internal stress, increasing the likelihood of cleavage cracking
- Precipitate formation is not affected by:
 - Growth Rate
 - Rotation Rate (Melt Circulation)
 - Crystal Furnace

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● Precipitate does not seem to be related to simple oxygen contamination

● Precipitate formation is not strongly affected by melt stoichiometry

The driving force for the creation of these scatter sites appear to be related to two possible mechanisms. The first and most likely due to impurity content in the raw materials resulting in a second phase formation at elevated temperatures. The impurity would probably tend to segregate to the melt upon solidification and would explain the scatter concentrating in the lower section of crystals. The second alternative would be that the second phase is intrinsic in nature, that is, a sub-solidus precipitation reaction that occurs in a defined temperature range. It is possible to quench small samples and not develop the second phase in this case.

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3.4 Process Improvements

The purity level of materials treated in Sanders' hydrofluorination system has improved by further optimizing process parameters. The improvements in the reaction cycle for processing has also reduced the furnace time for each batch from 48 to 24 hours.

The hydrofluorination system consists of a platinum lined ceramic tube, sealed at each end with teflon caps, situated in a Kanthal coil heated furnace. The feed is usually purchased as either oxide or carbonate powder and converted to the fluoride at a temperature below the melting point, using flowing anhydrous hydrogen fluoride gas. The converted fluoride powder is then melted under hydrogen fluoride in the cycle to complete conversion and reduce the bulk surface volume of the batch. The powders are placed in a rectangular platinum crucible, which in turn is placed on a graphite sagger. The graphite sagger prevents possible welding of the platinum crucible to the platinum tube.

Surface contamination of melts has been a continuous problem in crystal growth. Surface examination of sample melts by Auger spectroscopy, made during this program, identified the contaminants primarily as a mixture of carbon and oxides. Carbon contamination probably occurs during the hydrofluorination process, in which the reaction by-product, steam, attacks the graphite sagger. Rare earth oxides react with hydrogen fluoride in the following manner:

The by-product, water vapor, will attack the graphite sagger. Two approaches have been taken to reduce and eventually eliminate the attack on graphite. The initial action was to deposit a

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thin layer of pyrolytic graphite onto the graphite saggars. The anisotropic coating acts as a kinetic barrier to reduce the rate of attack. The reaction temperatures have also been lowered to reduce the activity of the water by-product. The majority of the reaction usually occurred at 1200°C , close to the melting point of most rare earths. The reaction temperature was reduced to 700°C to prevent the attack and the reaction time was extended to 48 hours. Both parameter changes have reduced the carbon contaminant produced by the fluorination reaction. Furnace cycle trials were then run, employing the mass flow meter and flow controller purchased on this contract, to optimize the cycle time. Given the amount of rare earth oxide to convert to fluoride, the minimum amount of hydrogen fluoride gas needed for conversion can be calculated. For 500 g of yttrium oxide, a minimum of 266 g. of HF is needed; flowing at 50g/hr, a minimum time of 5.3 hrs is required for complete reaction. The results of the experiments is that the fluoride conversion process at 700°C is close to stoichiometric, that is, only 10-20% excess HF is needed for the reaction, and the cycle time for each batch has been reduced to 24hrs.

Oxide inclusions have also been identified as a part of the surface contaminant. The argon used in the hydrofluorination process as well as for crystal growth is presently being scrubbed and monitored on the Centorr getter furnace purchased for this program. Oxygen content in the argon has been reduced well below 1 ppm.

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3.5 NEW MATERIALS

3.5.1 Introduction and Review of Previous Work

Most of the phase equilibria in the KF-REF_3 systems have been investigated (20-34). The work is characterized by general inconsistency.

Uniformly varying behavior as a function of rare earth ionic radius, that one would expect to find in rare earth chemistry, is missing from most reports on these systems. In sharp contrast to this is the simple behavior in the LiF-REF_3 (35) systems, whereas the size of the rare earth decreases, the systems progress from a simple type with a single eutectic and no intermediate compound to a more complex type with one intermediate compound (LiREF_4 starting at Eu) which progresses uniformly from incongruently to congruently melting. Similarly, but with greater complexity, the NaF-REF_3 systems (36) range from NaF-LaF_3 which is a simple type with one intermediate, incongruent but stoichiometric compound (NaLaF_4), to systems of increasing complexity as the rare earth becomes smaller in which a second nonstoichiometric solid solution compound appears. Isomorphism, with uniformly varying lattice constants is also a significant characteristic of the various compounds formed in these systems.

In the KF-REF_3 systems, the expected trends in the phase diagrams are not clearly established. For example, in the KF-CeF_3 (26) system a high temperature fcc solid solution phase in equilibrium with the melt is reported to lie between the composition limits KCeF_4 and KCe_2F_7 . Decomposition of the high temperature cubic phase occurs with formation of other phases, which in turn undergo changes as the temperature decreases. However, the bracketing systems, KF-LaF_3 and

KF-PuF_3 (20) are reported to be simple with one intermediate, incongruently melting phase (KREF_4).

More recent reports on the KF-YF_3 (25) system and on the KF-TbF_3 (21, 22) system indicate that cubic solid solutions are formed, but it is

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claimed that they are not equilibrium phases. Further inconsistencies are evident in the reported nature of compounds found in the KF-TbF_3 ($\text{KRE}_3\text{F}_{10}$) region. A compound $\text{K}_3\text{Tb}_5\text{F}_{17}$, cubic, $a_0 = 11.64\text{\AA}$ inverting to orthorhombic is reported in the KF-TbF_3 system. KY_3F_{10} is reported to be tetragonal, $\text{KEr}_3\text{F}_{10}$ to be monoclinic and $\text{KYb}_3\text{F}_{10}$ to be cubic at high temperatures, inverting to hexagonal at intermediate temperatures and back to cubic at lower temperature.

Schmutz⁽³⁴⁾ characterized KF/REF_3 compounds from Tb to Lu as having a cubic fluorite cell with $a_0 = 11.5\text{\AA}$ to $11.4\text{\AA}$ and compounds from La to Gd with a cubic cell of $5.9\text{\AA}$ but finds the compositions to be KRE_2F_7 . The data however are consistent in that the lattice constants vary in a regular and expected manner within each cubic structure type. Our discovery of two cubic phases in the KF-TbF_3 system is in agreement with Schmutz's observation of a change in structure type between terbium and gadolinium. For the heavier rare earths, Schmutz has characterized a cubic lattice constant variation with composition, which in our interpretation means that KRE_2F_7 is the KF rich limit and the $\text{KRE}_3\text{F}_{10}$ is the KF lean limit of the fcc solid solution. Further analysis of Schmutz's data would be uncertain. However, in sharp contrast to the Russian work, and in agreement with ours, he finds two homologous series of cubic rare earth compounds, stable at elevated temperatures.

Work in this laboratory on $\text{KRE}_3\text{F}_{10}$ compounds started with the appearance of a paper on $\text{KMRE}_3\text{F}_{12}$ ⁽³⁷⁾ (M is a transition metal) which we found to be nonexistent. Instead we crystallized KY_3F_{10} from a melt reportedly in equilibrium with $\text{KMnY}_3\text{F}_{12}$. Subsequently we grew small crystals of $\text{KTb}_3\text{F}_{10}$ and $\text{KEr}_3\text{F}_{10}$. Initial crystal growth⁽³⁸⁾ in the KF-TbF_3 system yielded a cubic material characterized as face centered from the indexed powder pattern, which contained only all odd or all even indices. The lattice constant was found to be $11.6\text{\AA}$. The x-ray and pycnometric densities agreed to within 1/2% with $Z = 8$ and a formula of $\text{KTb}_3\text{F}_{10}$. A chemical analysis of the analogous yttrium compound⁽²³⁾

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RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

(KY_3F_{10} and KTb_3F_{10} have virtually identical powder patterns) gave the composition as KY_3F_{10} . The first crystals of KTb_3F_{10} were grown from melts containing about 30 mol % KF as it appeared from earlier experiments that KTb_3F_{10} might be incongruently melting.

Using KTb_3F_{10} crystal chips as feed, which fixed the melt composition, it was found that the first phase to crystallize was TbF_3 . But as TbF_3 crystallized and the melt became enriched in KF, the KTb_3F_{10} field was entered, and this phase then was the only one crystallizing from the melt. The observed succession of phases crystallizing from the melt confirms the incongruent melting of KTb_3F_{10} . KF loss during this experiment was minimal and did not affect the results.

Further experiments in the $KF-TbF_3$ system were aimed at elucidating the phase equilibrium in systems containing greater than 30 mol % KF. The initial intent was to define the extent of the KTb_3F_{10} field and to bring some sense to the published phase diagram which did not agree with the results obtained in this laboratory. Crystals were then grown from the composition 35 mol % KF/65 mol % TbF_3 . Clear single phase material crystallized from the melt and remained clear while in contact with the melt. When cooled, however, a second phase precipitated in the crystal. X-ray and optical analyses showed the material to be a mixture of cubic KTb_3F_{10} and an unidentified second phase. To exclude oxide contamination as the source of the second phase, the crystal growth experiment was repeated several times using rigorously hydrofluorinated feed. Each time the same behavior was obtained, indicating that it was intrinsic and not the result of an oxide impurity.

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PUBLICATION NO

CLASSIFICATION

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3.5.2 Investigation of the KF-TbF_3 System

For the purposes of this work, the most important features of the KF-TbF_3 phase diagram are, the solid-liquid equilibrium at various melt compositions and the behavior of the crystals upon cooling from the growth temperature to room temperature. The method used in studying the phase equilibrium consists of growing on wire from a melt of known composition of a cylinder of material. This is normal freezing and from the succession of phases obtained along the length of the cylinder we can reduce the crystallization path and in some detail the phase diagram.

During growth of the Boule, its clarity and transparency is observed. Transparent growth, exclusive of surface etching indicates that the solid is a single phase. Phase transitions in the solid can be indicated by development of cracks as the crystal cools. Precipitation of a second phase can be seen as a development of opacity in material that had originally crystallized in clear form. High temperature phases can be preserved by quenching and by observing the crystal as it cools one can get a good idea from the appearance of the specimen, whether the rapid cooling has actually served to preserve the desired phase.

A transition during growth from a single phase field to a peritectic or eutectic point is typically marked in the crystal by a sharp very often mechanically fragile boundary below which two phases crystallize simultaneously. Three melt compositions were chosen for study, 55 mol-% KF , 50 mol-% KF and 40 mol-% KF . They were prepared from accurately weighed, hydrofluorinated TbF_3 and K_2CO_3 and HCO_3 .

55% KF /45% TbF_3

A small Boule was nucleated on a Pt wire, then disconnected from the melt and quenched by being pulled well above the melt into cooler

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PUBLICATION NO

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portions of the furnace; at the same time the furnace power was shut off. The crystal was clear during growth and remained so after being quenched. A small volume of material in contact with the Pt wire, however, was sufficiently cool to undergo a phase change. The clear portion of the boule appeared cubic under the polarizing microscope. Cleavage along the 111 plane could not be found and the powder pattern was indexed on a simple cubic cell of 5.74Å. The structure of this phase is closely related to that of $\text{KTb}_3\text{F}_{10}$ as the diffraction patterns of the two materials are very similar.

Some variation in lattice constant was observed for this phase as a function of the KF content of the melt. The largest lattice constant (least amount of KF) observed was 5.76Å. A plot of the lattice constants of Schmutz's cubic KRE_2F_7 against the trivalent ionic radius for La through Gd gives a smooth curve which extrapolated to Tb (Schmutz does not find this compound for Tb) yields a lattice constant of about 5.76Å.

The material crystallized at the Pt wire, principally monoclinic KTb_2F_7 , was assigned this composition on the basis of the agreement between its powder pattern and that reported for KDy_2F_7 (30).

A second crystal growth run was carried out using the same melt. In this case a 33mm long cylindrical boule grew with an enlarged bottom. The crystal started off clear, but as it grew it became opaque. The last portions were opaque as they grew, and by the end of the run the whole crystal was opaque. Remember that as the solid phase grows, the melt becomes enriched in KF. In the upper portion of the crystal that was clear during growth, the simple cubic phase, $a_0 = 5.74\text{Å}$ was present. Below the cubic phase was a two-phase region, containing KTbF_4 and KTb_2F_7 , which judging from the appearance of the boule during growth, formed as the cubic phase decomposed. Assignment of a composition to a powder pattern was made on the basis of published data. This two-phase region was terminated by a fragile boundary, below which was a region containing mainly small crystals of KTbF_4 .

LH FOLIO (EVEN)

CLA 123 ON

RH FOLIO (ODD)

PUBLICATION NO.

CLASSIFICATION

PUBLICATION NO.

at the bottom of the region was a single phase layer of millimeter size crystals of KTbF_4 . The very bottom of the crystals, separated from the rest by a sharp fragile boundary, was found to contain mainly well crystallized KTb_2F_5 .

50% $\text{KF}/50\% \text{TbF}_3$

A second set of experiments was carried out using a melt containing 50 mol % $\text{KF}/50 \text{ mol } \%$ TbF_3 . The first phase crystallizing from the melt was simple cubic with $a_0 = 5.74\text{\AA}$.

A second small boule was grown and cooled to room temperature over a one-hour period. The bulk of the boule remained clear and was found to be simple cubic but the shape of the diffraction lines indicates lattice strain.

While the crystal was growing, the material that formed first, that is the material directly in contact with and closest to the wire and therefore the coolest, lost some of its transparency but did not become opaque. X-ray analysis showed this material to be nearly single phase KTb_2F_7 .

A third small boule was crystallized from the same melt, clear when hot, but decomposing when cooled, at $20^\circ/\text{hr}$ to room temperature. X-ray phase analyses indicated that the material was mainly KTb_2F_7 and a cubic phase which could not be characterized as either simple or fcc without a detailed analyses of all the overlapping diffraction line shapes.

40% $\text{KF}/60\% \text{TbF}_3$

A small boule, clear while in contact with the melt, was grown and quenched. Unlike the other small quenched samples, this specimen cracked into mm sized pieces. The cracked surfaces did not appear to

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CL 124 ON

RH FOLIO (ODD)

PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

be cleavage planes. Under the microscope the material was cubic with some pieces showing strain but there did not appear to be a non-cubic phase. The powder pattern of this material could be indexed as a mixture of two cubic phases, one simple with a lattice constant of 5.76Å, and the other face centered with a lattice constant of 11.60Å. Unstrained cubic pieces were selected and found to be the face centered phase, while those pieces showing more strain were the simple cubic phase, but showing some signs of the beginning of a transformation.

Strained cubic pieces were reheated to near the melting point and cooled to room temperature at about 20°/hour. The specimen became non-cubic but a trace of cubic phase was seen under the microscope.

Identification of the non cubic phase could not be made. However, it is the same phase that precipitated from $\text{KTb}_3\text{F}_{10}$ solid solutions crystallized from melts containing 35% KP.

Density and Lattice Constant Measurements of $\text{KTb}_3\text{F}_{10}$

It is fairly clear that over the range of compositions studied, a cubic solid solution is in equilibrium with the melt. Only face centered cubic material, however, was available in sufficient quantity and quality to be used for pycnometric density measurements. The solid solution is KP rich relative to $\text{KTb}_3\text{F}_{10}$ and is formulated as $\text{K}_{1+x}\text{Tb}_{3-x}\text{F}_{10-2x}$. Using this formulation we have

$$\text{KTb}_3\text{F}_{10} = \text{KTb}_3\text{F}_{10}$$

$$\text{KTb}_2\text{F}_7 = \text{K}_{1.33}\text{Tb}_{2.67}\text{F}_{9.34}$$

The lattice constant and unit cell volume were calculated from the 888 reflection of a cleaved specimen, and used without refinement. Densities were measured on carefully selected, transparent, inclusion free specimens using a one cc pycnometer. Weighings were done a Mettler balance.

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PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

Top and Bottom pieces of Boule #546 were analyzed in order to assess the lattice constant change as the melt was enriched in KF during a growth run. Lattice constants, densities and formulas for the top and bottom respectively were 11.671A, 5.776 g/cm³ and $K_{1.09}Tb_{2.91}P_{9.82}$ and 11.669A, 5.752 g/cm³, and $K_{1.11}Tb_{2.89}P_{9.76}$. KTb_3P_{10} regrown close to the peritectic composition from KTb_3P_{10} crystals has the formula $K_{1.03}Tb_{2.93}P_{9.93}$, a lattice constant of 11.674A and density of 5.85 g/cm³. Lattice constant measurements on

other samples have been used to diagnose crystal growth problems relating to the KF constant of the melts. There is a correlation between decreasing lattice constant, increasing KF in the crystal and increasing amount of KF in the melt and decreasing stability of the KTb_3P_{10} solid solution.

Summary of the $KF-TbF_3$ Phase Diagram

Five different phases have been found to be in equilibrium with $KF-TbF_3$ melts over a composition ranging from somewhat greater than 55 mol % KF to 25 mol % KF. From 27 to 0% KF the primary phase is TbF_3 . From 27 to 40% a face entered cubic solid solution with the formula $K_{1+x}Tb_{3-x}P_{10-2x}$ crystallizes. The limiting KF lean composition for this phase is KTb_3P_{10} . Between 40 and 55 mol % KF, the melt is in equilibrium a simple cubic phase. At a composition less than but close to 55% KF hexagonal $KTbF_4$ crystallizes, but over a narrow composition range. At a slightly richer KF content KTb_2F_5 and a second unidentified phase form. Under the microscope this material shows an eutectic structure. The liquidus temperature was not measured directly but judging from the system temperature during the crystal growth experiments, the liquidus temperature falls monotonically with increasing KF concentration.

Both cubic solid solutions decompose at uncharacterized temperatures possibly only a few hundred degrees below the liquidus temperature.

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PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

ture. The rate of decomposition of the solid solution increases with increasing KF content. The $\text{KTb}_3\text{F}_{10}$ solid solution decomposes to $\text{KTb}_3\text{F}_{10}$ and an uncharacterized second phase. It is apparent from the X-ray powder patterns that this second phase is poorly crystallized, and it may not be an equilibrium phase. The simple cubic phase decomposes to KTb_2F_7 and KTbF_4 with the proportion of the former being very high when the melt contained 50% KF and being nearly 100% KTbF_4 when the melt contained a little more than 55 mol % KF. A phase diagram based on these observations is presented in Fig. 57. 57

The implication of this diagram is that growth of $\text{KTb}_3\text{F}_{10}$ must be carried out from melts containing the minimum necessary amount of KF. With a small excess of KF, the $\text{KTb}_3\text{F}_{10}$ solid solution is stable enough to be grown and cooled to room temperature without decomposition. Crystal growth from melts richer than about 30% KF leads to formation of a solid solution too unstable to be preserved other than by quenching.

Many details of the phase equilibria remain unresolved, in particular, the way in which the $\text{KTb}_3\text{F}_{10}$ solid solution decomposes. Also the shape of the liquids and the various transition temperatures remain in doubt. However, a sound framework has been developed which can serve as an accurate guide to a more detailed investigation.

3.5.3 Europium Difluoride

EuF_2 was investigated as a possible faraday rotator material. EuF_2 is a cubic material, as such, it exhibits a potential for application of hot forging techniques to expand aperture size. The following study includes reduction of EuF_3 to EuF_2 and crystal growth of EuF_2 .

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Phase Diagram for the $\text{KF} - \text{TbF}_3$ System

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KF-TbF₃ SYSTEM

NOTES:

1. The temperature scale is approximate and not to scale.
2. The subsolidus decomposition schemes shown are only suggestions about what might be occurring.
3. Phase E, although uncharacterized, is introduced to provide a scheme for accounting for the coexistence of ss and ss₂, and decomposition of ss to KTb₃F₁₀ and Phase E.

4. Phase fields,

ss₁ face centered cubic solid solutionss₂ simple cubic solid solutiona ss₁ + uncharacterized non cubic phase Eb ss₁ + cubic KTb₃F₁₀c ss₂ + hexagonal KTbF₄d ss₂ + monoclinic KTb₂F₇e KTb₂F₇ + phase Ef ss₂ + phase Eg fcc KTb₃F₁₀ + phase E51
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PUBLICATION NO.

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Synthesis of Europium Difluoride

Europium trifluoride obtained from Research Chemicals was hydrofluorinated at 750°C in an Inconel reactor prior to reduction. Solid EuF_3 was reduced to EuF_2 with hydrogen according to the reaction:

The charge was contained in a vitreous carbon boat in the same apparatus as was used for hydrofluorination. In the first experiments, forming gas, argon - 5% hydrogen, was the reductant. At 800°C, very little reaction took place over a several hour period. When the reduction was carried out at 1000°C, however, the yield of EuF_2 rose to about 50% for about a four and a half hour reaction time.

A third reduction of the same charge was carried out in pure hydrogen at 1000°C, resulting in about an 80% yield of EuF_2 as judged from the x-ray powder pattern. Some sintering occurred during the hydrogen reduction process, which may have prevented complete reaction of EuF_3 with hydrogen to form EuF_2 .

Experiments involving reduction of molten LiF-EuF_3 with hydrogen were conducted in order to develop a means of avoiding a sluggish solid state reaction. A molten mixture of 50 mole % LiF , 50 mole % EuF_3 was treated in hydrogen at 1000°C for about three hours. The unreduced mixture melts at about 700°C and it is felt that the fully reduced mixture should melt in the vicinity of 900°C. Assay by weight loss of the product of this reduction experiment indicated only a 36% yield of Eu^{2+} . The x-ray powder pattern of the material shows the presence of EuF_3 , as well as of EuF_2 , and suggested a similar ratio. Brown crystals were also isolated from the frozen melt, which are probably an $\text{EuF}_2\text{-EuF}_3$ solid solution. It has not yet been determined whether incomplete reduction is simply a result of too short a reaction time or whether formation of EuF_2 raised the melting point of the system to above 1000°C thus causing solidification.

PUBLICATION NO.

CLASSIFICATION

PUBLICATION NO.

There is no question about the ability of hydrogen to reduce Eu^{3+} to Eu^{2+} . The problems encountered here are undoubtedly due to kinetic factors and can be solved either through longer reduction times or higher temperatures, or both.

Crystal Growth of EuF_2

Using the feed prepared by hydrogen reduction of solid EuF_3 , crystal growth runs were carried out from EuF_2 , EuF_2 containing 10 mole % MgF_2 , and EuF_2 containing 50 mole % LiF . Crystallization in the unfluxed EuF_2 run was nucleated on a platinum wire at about 1570°C . A brown, non-cubic, EuF_2 solid solution was obtained. The powder pattern indicates some distortion from cubic EuF_2 , but further characterization was not possible. If crystal growth is to be carried out from the stoichiometric melt, a significantly more pure EuF_2 will be required.

Flux growth of EuF_2 can assist by diminishing the various problems presented by growth from the stoichiometric melt. For one, temperatures will be lower, and possibly incorporation in the crystal of EuF_3 will also be diminished as a result of the lower temperatures. Divalent europium is chemically similar to barium; therefore, initial choices of flux were made on the basis of published barium fluoride phase diagrams, with MgF_2 and LiF as the two initial flux choices. Small amounts of MgF_2 greatly lower the melting point of BaF_2 .

A second crystal growth experiment was carried out using the EuF_2 prepared by solid state reduction of EuF_3 fluxed with 10 mole % MgF_2 , again nucleated on a platinum wire, but at 1275°C , three hundred degrees lower than in the unfluxed system. Failure of the control thermocouple, however, imposed a premature end to this experiment. A small piece of crystalline material was recovered and found to be brown and non-cubic.

This and the previous melt was opaque at the respective crystal growth temperatures, a factor which works against growth of good quality crystals. Radiation from the melt surface changes the thermal condition of the melt such that the crystal melt interface becomes concave, introducing problems ranging from grown-in strain to difficulty in control of the crystal diameter. The concavity can be lessened, and even reversed, by decreasing the rotation rate at which the crystal is grown. However, in these experiments, a rotation rate of 10 rpm was still not sufficient to effect this reversal. It was felt, then, that an even lower melting point system should be sought out.

Projecting from the BaF_2 -LiF system, LiF should lower significantly the melting point of EuF_2 . An additional interesting and potentially very useful feature of the LiF- EuF_2 system is the possibility of the existence of LiEuF_3 , which, if similar to the barium compound, will be cubic and incongruently melting. Growth of this hypothetical LiEuF_3 should provide an excellent means of purifying EuF_2 with respect to trivalent europium. This compound may be interesting itself, or, in incongruently melting, could be recrystallized to yield a high purity EuF_2 . For a third crystal growth experiment, a melt containing 50 mole % LiF was prepared, using EuF_2 prepared by hydrogen reduction and neglecting the EuF_3 content. This mixture melted at around 1050°C , and crystal growth was grown and was found again to be an EuF_2 solid solution. The material is still non-cubic, but the splittings shown in the x-ray diffraction pattern are smaller than for the crystal obtained from the pure and magnesium fluxed experiments. The material remaining in the crucible after removal of the small crystal was examined by x-ray diffraction and found to contain, in addition to this EuF_2 solid solution, a small amount of LiEuF_4 . So far the presence of LiEuF_3 has not been detected in either this preparation or in the LiF- EuF_3 melt directly reduced by hydrogen. Use of an LiF flux appears quite promising, but proper evaluation will have to await the preparation of a completely reduced melt.

PUBLICATION NO

CLASSIFICATION

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3.6 PROPERTIES OF YLF AND KYF

3.6.1 dN/dT for YLF

The effect of temperature on the index of refraction was measured for undoped $LiYF_4$ from 5° to $50^{\circ}C$. The values of dN/dT at wavelengths of 442nm, 633nm, and $1.06\mu m$ are reported in Table 6. In addition, values for some laser pumped glasses are reported. dN/dT in both directions of $LiYF_4$ are comparable to presently used glasses.

3.6.2 Properties of KYF

Samples of KYF grown for this program were prepared and delivered to the Laboratory of Laser Energetics, University of Rochester; and The Material Science Center, Honeywell Corporation. The properties to be measured at the University of Rochester include: refractive index, physical density, $\delta n/\delta t$, thermal conductivity, optical density and thermal expansion. Samples on Table 7 list the properties that have been measured. KYF sent to Honeywell will be used to perform not forging experiments.

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TABLE 6

CHANGE IN THE REFRACTIVE INDEX AS A FUNCTION OF TEMPERATURE BETWEEN
5° AND 50°C FOR YLF AND OTHER LASER HOSTS (37)

WAVELENGTH	442nm ($\times 10^{-6} \text{ } ^\circ \text{C}^{-1}$)	633nm ($\times 10^{-6} \text{ } ^\circ \text{C}^{-1}$)	1060nm ($\times 10^{-6} \text{ } ^\circ \text{C}^{-1}$)
------------	---	---	--

YLF Polarization in "c" direction	-3.0	-3.0	-4.3
--------------------------------------	------	------	------

YLF Polarization in "a" direction	-0.8	-1.6	-2.0
--------------------------------------	------	------	------

ED-2	---	+3.0	+3.1
------	-----	------	------

Q-88	---	+0.5	+1.6
------	-----	------	------

LHG-7	---	-2.9	-2.6
-------	-----	------	------

YAG	---	---	+7.3
-----	-----	-----	------

Ruby	---	+12.6	---
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[illegible]~~PROPERTIES OF KYF (KYF₃/10)~~

CUBIC (MODIFIED FLUORITE)

DENSITY (gm/cm³)

4.38 (38)

THERMAL CONDUCTIVITY, W/cm⁰K

0.027 (38)

INDEX OF REFRACTION

$$\lambda = 1.0$$

1.48

NONLINEAR INDEX (10^{-13} esu) $\sim 0.6 (39)$

UV-VIS ABSORPTION

 $< 0.300 \text{ nm}$

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PUBLICATION NO

CLASSIFICATION

PUBLICATION NO.

CONCLUSION:**4.0 CONCLUSION**

The work during this program has led to significant developments in the field of laser materials and high power laser systems. Two particularly critical milestones in the development of solid state lasers for inertial confinement fusion have been obtained, demonstration of a rare gas halide pumped solid state storage laser and fabrication of large single crystal laser material. Both accomplishments have established a technology baseline to be expanded upon in future programs.

The system combination of a rare gas halide laser pumping a solid

state laser is predicted to obtain the high levels of energy, efficiency, and peak power required for fusion drivers. Sanders has predicted and demonstrated the XeF-Tm:YLF laser system. Overall conversion efficiency is predicted to be between 40 and 50%. Further investigation into this system is warranted to validate system efficiency, measured heat loading, and determine the accuracy of the energy transfer model. More efficient RGH: solid state storage systems should also be investigated. Solid state system capable of storing KrF laser energy are of interest, as a KrF laser is about twice as efficient as an XeF laser. As such, total system efficiency may improve. Further experimentation will be required to demonstrate such systems.

The crystal growth of 10cm diameter single crystal YLF is very significant in the development of laser materials. The crystals grown for this program are the largest single crystal fluorides fabricated by TSSG techniques. The versatility of YLF for active and passive components creates a tremendous potential for this material in high power lasers. Laser fusion application requires material in diameters of 20 to 40 cm. The initial scaling of crystal growth of YLF has been successful. Further development will be required to expand growth facilities and technology to meet the demand for efficient, high powered fusion drivers.

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CLASS 136 ON

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CLASSIFICATION

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APPENDIX A

PULSE DELAY AND UPPER STATE DECAY

After an upper state population has been created, a period elapses while the laser pulse builds from spontaneous emission.

The delay time is given by the formula:

$$\tau_D = \left[\frac{2L}{c} \right] \left[\frac{E_{TH}}{E_p - E_{TH}} \right] \tau_0$$

where

L = Cavity optical path length

c = speed of light

E_{TH} = Necessary pump energy for threshold

E_p = Pump energy for the particular case

and

τ_0 = A unit of delay time derived from the rate of spontaneous emission into the beam volume

It can be seen that as E_p approaches E_{TH} , τ_D becomes large. If τ_D approaches τ , the upper state lifetime, a significant fraction of the stored inversion will decay in this delay interval. For the case of the Tm:YLF resonator of Figure 1

$$\tau_D \approx 40 \left(\frac{E_{TH}}{E_p - E_{TH}} \right) \text{ nsec}$$

Therefore at 10% over threshold

$$\tau_D \approx 400 \text{ nsec}$$

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and at 5% over threshold

$$\tau_D \approx 800 \text{ nsec}$$

Therefore as threshold is approached, very large decay losses set in. The above correspond to 35% and 55% losses respectively for 10% Tm:YLF (a concentration many times that of an operational amplifier element). This tends to "round off" the slope efficiency curve, making it remain at zero past where the extrapolated zero output intercept would be. It is easy to calculate that this effect increased the measured threshold by ~25%. The effect also makes the slope efficiency anomalously high on the 'knee' of an energy out vs energy in plot.

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APPENDIX B

LOWER LEVEL BOTTLENECKING AND SATURATION FLUX

Points previously not well understood were the effect of lower level bottlenecking on extraction efficiency n_{ex} and saturation flux E_{SAT} .

The limiting extraction efficiency is calculated using the following argument: the gain in the crystal at any moment is:

$$g = \sigma (\beta_u N_u - \beta_L N_L)$$

Where:

σ is the stimulated emission cross section
 β_u and β_L are the upper and lower level occupation factors respectively
 N_u and N_L are the upper and lower manifold number densities respectively

The lasing is presumed to commence with an original upper manifold population of N_u and no lower manifold population. The laser "shuts down" when the gain is zero or

$$g = 0 = \sigma (\beta_u N'_u - \beta_L N'_L)$$

so

$$\beta_u N'_u = \beta_L N'_L$$

The fraction of the energy extracted is

$$n_{ex} = \frac{N_u - N'_u}{N_u}$$

and as $N'_u + N'_L = N_u$, as there is assumed to be only stimulated transitions in the short period during which the output pulse is generated.

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$$\begin{aligned}
 n_{ex} &= N_L' / (N_u' + N_L') \\
 &= N_L' / \left(\frac{\beta_L}{\beta_u} N_L' + N_L' \right) \\
 &= \beta_u / (\beta_u + \beta_L)
 \end{aligned}$$

The extractable energy Q is originally

$$Q = N_u h\nu \beta_u / (\beta_u + \beta_L)$$

where $h\nu$ is the energy of one output photon. This is equal to the product of the gain g , and the saturation flux, E_{SAT} as

$$Q = E_{SAT} g,$$

so

$$\begin{aligned}
 E_{SAT} &= Q/g \\
 &= \frac{N_u h\nu \beta_u}{(\beta_u + \beta_L)} \\
 &= \frac{N_u \sigma \beta_u}{\beta_u \sigma} \left(\frac{\beta_u}{\beta_u + \beta_L} \right)
 \end{aligned}$$

For the observed transition in Im:YLF, assuming a cross section occupation

$$\beta \sigma = 3.2 \times 10^{-20}$$

$$E_{SAT} = 10.7 \text{ J/cm}^2$$

Using the experimentally derived lower limit of $\sigma \geq 1.9 \times 10^{-19} \text{ cm}^2$

$$E_{SAT} \leq 18 \text{ J/cm}^2$$

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Again this is an upper limit but it should be within a factor of two, and although little design criteria for large systems have been arrived at, this is an appropriate value for a high energy, nano-second regime, efficient laser amplifier.

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