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NEW LASER MATERIALS FOR LASER DIODE PUMPING
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Introduction

The potential advantages of laser diode pumped solid state lasers are many, high overall efficiency being the most important. The other advantages include long life, lower differential heat load in the active material and a more compact system. In order to realize these advantages however, the solid state laser material needs to be optimized for diode laser pumping and also for the particular application. In the case of the Nd laser, materials with a longer upper level radiative lifetime is desirable. This is because the laser diode is fundamentally a cw source and to obtain high energy storage a long integration time is necessary.

In this program we are investigating fluoride crystals as host materials for the Nd laser and also for IR laser transitions in other rare earths, such as the $2\mu m$ Ho laser and the $3\mu m$ Er laser. The approach is to investigate both known crystals, such as BaY_2F_8, as well as new crystals such as $NaYF_4$. In this reporting period we have concentrated on the growth and spectroscopy of BaY_2F_8. These two efforts are paralel efforts. The growth effort is aimed at establishing conditions for obtaining large, high quality boules for laser samples. This requires numerous experimental growth runs, however, from these runs samples suitable for spectroscopy become available.

Energy Transfer in Er,Pr:BaY$_2$F$_8$

The phenomena of energy upconversion and its impact on solid state laser performance is presently an area of intensive research. This is partly due to the fact that the upconversion has been exploited to overcome the long lifetime of the $^4I_{13/2}$ terminal laser level of the $3\mu m$ Er laser, allowing CW operation in a material that should have been self terminating. In contrast, upconversion is thought to limit the power available from 2 micron Tm and Tm, Ho lasers . Because the strength of upconversion is proportional to the square of the excited population, it becomes a rapidly increasing loss when the material is strongly pumped.

Energy transfer is thus a two edged sword: it can increase efficiency and even make CW operation possible for transitions that would otherwise self terminate, but it can also limit the efficiency of a laser, especially at high pump powers. Unfortunately, it is difficult to

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determine the effects of upconversion for a given system because the physics of such a process are somewhat complicated. For two excited atoms to "upconvert", they must be near each other as the weak interaction falls off rapidly at longer distances. This would imply that upconversion is important only under very strong pumping, where a large proportion of the ions are in the excited state. Yet upconversion effects can be seen even under moderate pumping (1-10% excited population) because the energy can migrate through the donor ions, so that the excitation can reside on many (10^4 ? , 10^6 ?) different ions in search of another nearby excitation. This diffusion is also strongly dependent on the distance between nearest donor ions, and accounts for the use of high concentration (greater than 10%) of Er used in the 3 μm lasers.

To determine the strength of the upconversion it is necessary to understand the process whereby the excitation diffuses throughout the lattice. There has been much theoretical and experimental work on the microscopic physics of energy diffusion, but it has generally been carried out in lightly doped samples, where many simplifying assumptions allowed a more rigorous theoretical solution of the problem. [1], [2] In addition, the results of previous measurements on upconversion in high concentration Er:YLF indicate that the strength of the upconversion has an unexpected dependence on concentration that we think may be due to the concentration dependence of the diffusion process. [3]

To measure the diffusion concentration dependence, we have started a series of measurements on different concentrations of Er:BaY$_2$F$_8$ doped with small amounts of Pr. The Pr ions act as quenching centers for the Er excitations, so that the excitation can diffuse through the Er lattice until transferring to a Pr ion, where it is rapidly quenched by non-radiative relaxation in the Pr. We observe the effect of the Pr by measuring the lifetime of the Er decay; with larger amounts of Pr, the excitation must diffuse a shorter distance to reach a Pr ion, and so the decay will be faster. By measuring the decay for many of the different Er levels , we can try to evaluate the diffusion dependence on levels with different lifetimes.

The samples are prepared in a long boat partially filled with a uniform charge of Er:BaY$_2$F$_8$. (See figure 1.) On top of this is placed Pr:BaY$_2$F$_8$ powder, with more powder at one end of the boat than at the other. The boat is put into a zone refiner (a moveable furnace with a narrow hot zone), which melts the Er:BaY$_2$F$_8$ and the Pr:BaY$_2$F$_8$ together, but only over a narrow slice. After one pass of the hot zone over the length of the boat, it is possible to get a gradient of Pr coexisting with uniform Er doping. The polycrystalline material is then cut into thin slices and the relative Pr content measured using the polarized absorpion spectra

of each slice. The concentration is absolutely calibrated by dissolving one sample and comparing the absorption to an aqueous solution of known Er and Pr concentration. We have used this technique to prepare samples with 1%, 5%, 20% and 50% Er:BaY$_2$F$_8$.

At present we have completed initial lifetime measurements on two sets of samples: 5% Er: BaY$_2$F$_8$ and 20% Er:BaY$_2$F$_8$ with Pr concentrations from 0.05% to 1.5%. The $^4I_{13/2}$ lifetimes for both sets of samples was measured by pumping directly into the 13/2 level with short pulses of 1.54μm light from a Raman shifted Q switched Nd:YAG laser. The $^4I_{11/2}$ and $^4I_{9/2}$ lifetimes were measured by pumping the 9/2 level with a pulsed Ti:Sapphire laser. For the 11/2 and 13/2 lifetimes, the decay was completely exponential, indicating that diffusion was very efficient at removing any local variation in the environment of the Er ions. The 9/2 level, with a much shorter lifetime, exhibited non-linear decay because the short lifetime did not allow much diffusion, so that Er ions near to Pr ions relaxed faster than those without a Pr ion nearby. In addition, the 9/2 level can decay by cross-relaxation to the 13/2 level which also leads to non-exponential decay.

The rate of decay (1/lifetime) can be plotted vs. the concentration of Pr in the crystal to get the diffusion coefficient. For both the 13/2 and 11/2 levels in both 5% and 20 % Er series, the rate (inverse lifetime) was linearly proportional the the concentration of Pr ions in the sample. (See figs 2 & 3.) This is predicted by the theory on energy transfer with diffusion, and the relevant expression describing the decay rate is [1]:

$$\frac{1}{\tau} \cong 8.5 \ N_{Pr} C^{1/4}_{Er-Pr} D^{3/4}$$

where N$_{Pr}$ is the Pr concentration and $\dot{C}_{Er-Pr}$ is the microparameter for transfer from the Er to the Pr, which can be calculated [4] from the singly doped Er lifetime τ, the integrated Pr absorption cross-section Q, and the overlap of the Er emission and Pr absorption lineshapes f(E) :

$$C_{Er-Pr} = \frac{3}{4\pi} \left(\frac{\hbar c}{n}\right)^4 \frac{Q}{\tau} \int f(E)^{Pr}_{abs} \ f(E)^{Er}_{emit} \frac{dE}{E^4}$$

We have measured:

20% Er, $^4I_{13/2}$:   C = 1.12 10^{-38} cm^6/sec   D = 6.1 10^{-10} cm^2/sec

5% Er, $^4I_{13/2}$:   D = 0.62 10^{-10} cm^2/sec

With only a few data points, it is hard to say much about the concentration dependence of the diffusion coefficient D.   Ref [5]   predicts that $D^{3/4}$ should be linear with the concentration of donor ions. For the above values, the ratio of $\{D(20\%)/D\ (5\%)\}^{3/4} = 5.5$, which is slightly greater than the ratio of the concentrations (4:1). This would suggest that diffusion may be more efficient than expected at high concentratios, perhaps due to the fact that at 20% almost all Er ions have at least one nearest neighbor, so that all of the interactions that lead to diffusion happen over the same short distance. We expect a change in the diffusion efficiency as the concentration reaches a threshold value, in analogy with the onset of percolationwith the formation of large clusters in two phase materials [6].

We are presently completing work on 1% Er and 50% Er samples with a range of Pr. This should give a larger range of Diffusion coefficients to work with, allowing a more accurate look at the concentration dependence of D. In addition, we will extend the measurement to the $^4F_{9/2}$ and $^4S_{3/2}$ levels, so that we will be able to compare the diffusion across 5 different levels, with lifetimes from 10 msec to 10 μsec.

Crystal growth of RE:BaY$_2$F$_8$

The issues to be addressed in the crystal growth study are :

i) growth orientation, thermal gradients in the furnace, seed rotation and pulling speed

ii) purity of feed material and the growth atmosphere

iii) formation of grain boundaries during the growth

Issues i) and iii) are related to thermal stress in the crystal and consequently to the optical quality. The issues in ii) are related to scattering centers in the crystal due to the formation of secondary phases involving oxygen or other impurities, and in this way they also affect the optical quality of the crystal.

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Program Plan

<u>1</u>   Growth of spectroscopic samples of RE^{3+} doped BaY_2F_8

<u>2</u>   Growth of laser boule size crystals of Nd doped BaY_2F_8

<u>3</u>   Optimization of growth parameters for Nd doped BaY_2F_8

The following BaY_2F_8 crystals were grown:

Run #	*Doping*	*Purpose*	*Seed direction*
22NF:	5%Tm	spectroscopic sample	(0 0 1)
22NF(a):	5%Tm	spectroscopic sample	(1 0 0)
25NF:	2.5%Nd	laser boule	(1 0 0)
27NF:	2.5%Nd	laser boule	(1 0 0)
27NF(a):	2.5%Nd	laser boule	(1 0 0)
27NF(b):	2.5%Nd	laser boule	(1 0 0)
581F:	5%Tm	spectroscopic sample	(1 0 0)
581F(a):	5%Tm	spectroscopic sample	(1 0 0)

Experimental   conditions:

1)Thermal gradients study : The crystals named NF and F were grown in two distinct furnaces. The thermal gradients are different for both furnaces. The thermal gradient for the same furnace can also be modified by changing the furnace set up, using, for example, a Pt crucible inside a graphite cup or a vitreous carbon crucible by itself. The Tm-doped crystals were grown in platinum crucibles and the Nd doped crystals in vitreous carbon crucibles with double of the amount of feed usually used in previous experiments. We are

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not sure as yet how the difference in thermal gradients will affect the crystal quality. However, it seems that the radial temperature is more uniform in the second case.

Seed orientation : Crystals were grown in two new directions: (100) and (001). Previously only crystals in the (010) direction had been grown.

Seed rotation and pulling rate : These factors do not seem greatly affect the crystal quality in the range of 0.5 to 1.0mm/hr for pulling and 15 to 25 rpm for rotation.

2)Feed preparation,purification and growth atmosphere-The starting materials for the feed used in all the runs were: Y_2O_3 and dopant Ln_2O_3 (Research Chemicals 99.999%) and BaF_2 (Optovac optical grade).The components were mixed together and hydrofluorinated, with maximum temperature of 1100 C. Further purification by zone-refining the fluoride in HF atmosphere did not improve the crystal quality but showed that some of the scattering centers present in BaY_2F_8 are related to poor temperature control and not to feed purity.

Temperature control : In the furnace "NF", the temperature can be monitored during the run such that if any temperature perturbation occurs during the run it can be related to defects in the crystals.

Results

Comparing crystals grown in the same experimental conditions but for the seed orientation, we came to the conclusion that cracking is more severe for crystals grown in the (001) direction and much less or inexistent for crystals grown in the (100) direction. See figures 4 and 5. This makes sense when we take in consideration the values for the thermal expansion coefficients measured for the three directions[7]:

a-17, b-18.7, c-19.4x10^{-6} K^{-1}.

The growth conditions seem to be better for furnace "NF" than for "F". The crystals grown in the (100) direction are less crooked in the first furnace. Nd: BYF crystals were all straight. See figure 6. Since in this furnace we can monitor diameter and temperature during the growth we can adjust the control parameters during the run, in order to correct any fluctuations in power.

Bubbles present in crystals can be traced to perturbations in the temperature due to diameter control. This also occurs for YLF crystals and is not related to purity of feed or growth atmosphere.

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Any "scum" present on the surface of the melt might contribute to formation of grain boundaries during seeding. Necking the crystal after "scum" pick up solves the problem of grain boundaries but if the growth direction is (100) the crystals might grow crooked.

Crystals grown in this program showed great improvement compared to crystals grown before in this same laboratory. The crystal 22NF, for example, when inspected with a laser He-Ne does not show any diffuse scattering or hardly any bubbles. The Nd-doped crystals also do not display diffuse scattering. In addition, they do not crack as readily as they used to when grown in the (010) direction.

Study of the growth of $NaLaF_4$

Based on our work on the growth of $NaYF_4$ we tried to grow its analog, $NaLaF_4$ and verify if the growth of single crystals was easier than for $NaYF_4$. The phase diagram is basically the same for $NaYF_4$. We used a starting composition of 60%NaF and 40% YF_3, which according to the phase diagram data should yield $NaLaF_4$ as the first phase to crystallize from the solution. However, the material crystallized on a Pt wire when examined by X-ray diffraction revealed to consist of a mixed phase of $NaLaF_4$ and LaF_3. We proceeded pulling more material from the melt and finally got to a region where $NaLaF_4$ was the only phase to be crystallized. Consequently the phase diagram is incorrect. The crystal growth is indeed different from the growth of $NaYF_4$, but not easier. The lifetime of a Nd-doped sample was measured to be about the same value for $Nd:NaYF_4$.

Growth of YLF single crystals

In addition, the following crystals were grown:

run # 580F: YLF: 5%Tm:0.2%Ho

run # 580F(a):   YLF: 5%Tm:0.2%Ho

run # 580F(b):   YLF: 5%Tm:0.2%Ho

The starting materials for the feed used in all the runs were: Y_2O_3 (Research Chemicals 99.999%), Nd_2O_3 (Research Chemicals 99.99%) and LiF (Harshaw optical grade).

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P.B. deGennes, J. Phys. Chem. Solids **7**, 345 (1958).

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D.L. Dexter, J. Chem. Phys. **21**, 836 (1953).

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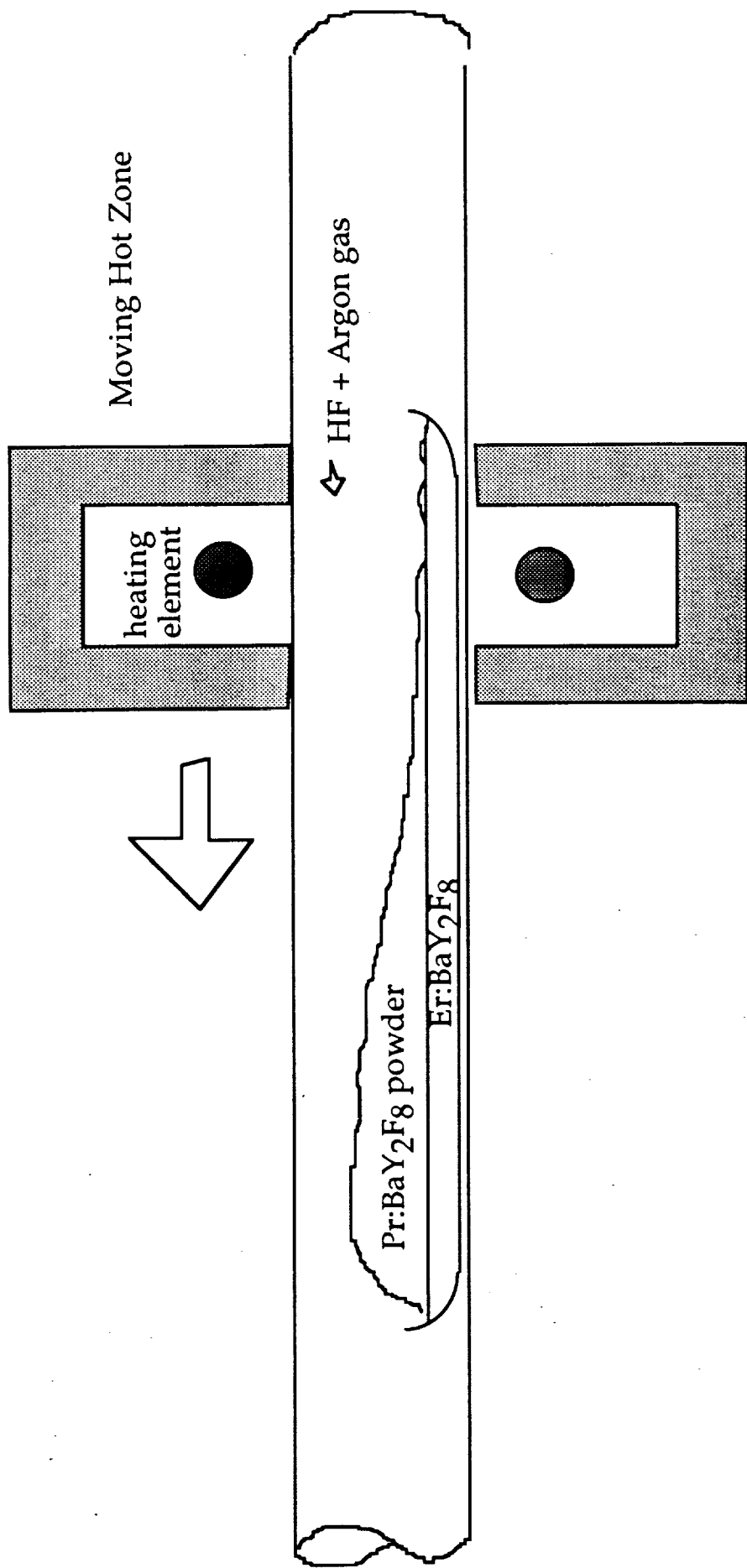
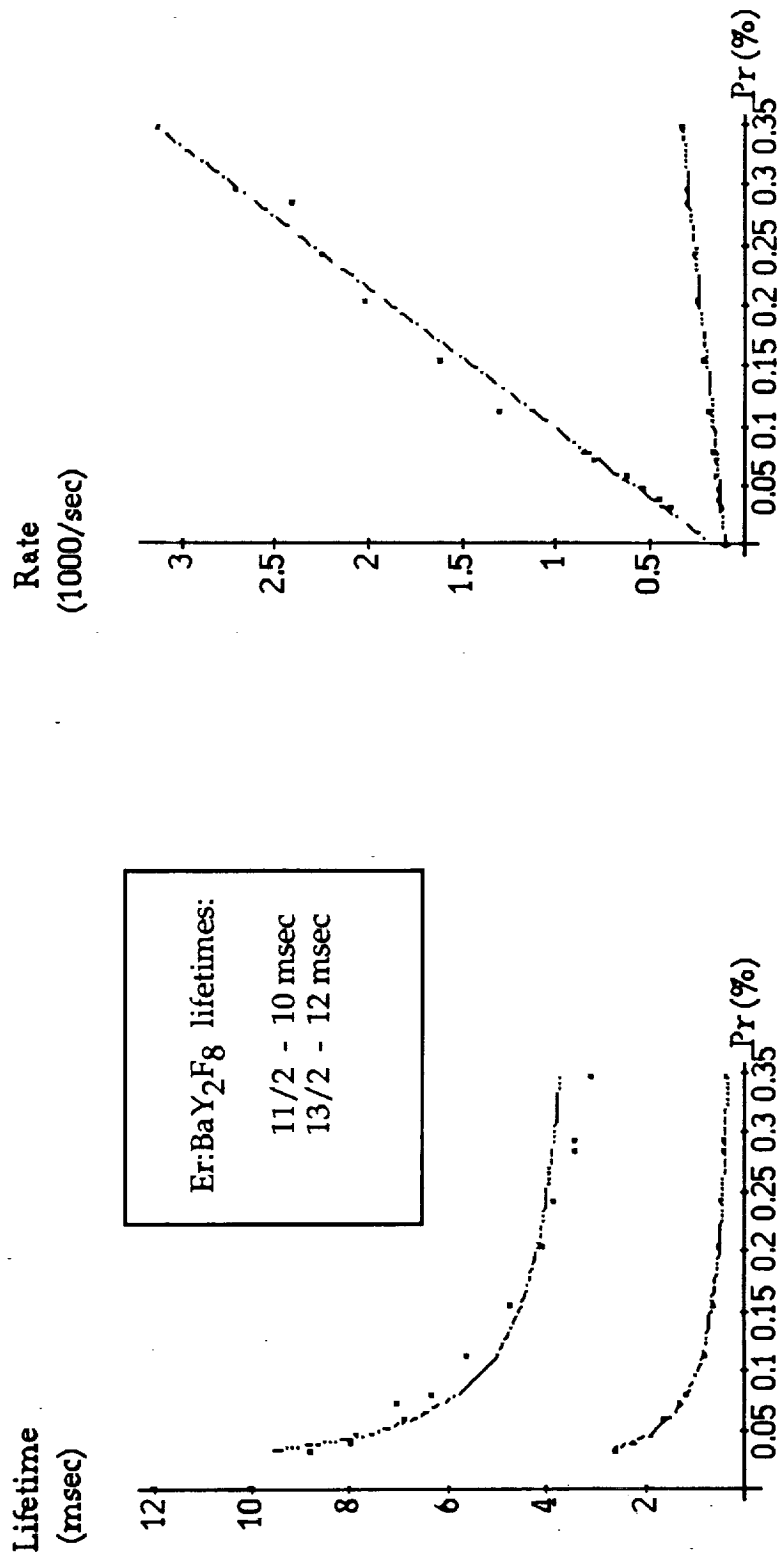Figure 1. Preparation of Er, Pr:BaY$_2$F$_8$ samples using Zone Refiner

5% Er: BaY$_2$F$_8$ Codoped with Pr

Rate
(1000/sec)

Pr (%)

Er:BaY$_2$F$_8$ lifetimes:

11/2 - 10 msec
13/2 - 12 msec

Lifetime
(msec)

Pr (%)

Figure 2. Quenching of Er by Pr

20% Er: BaY$_2$F$_8$ Codoped with Pr
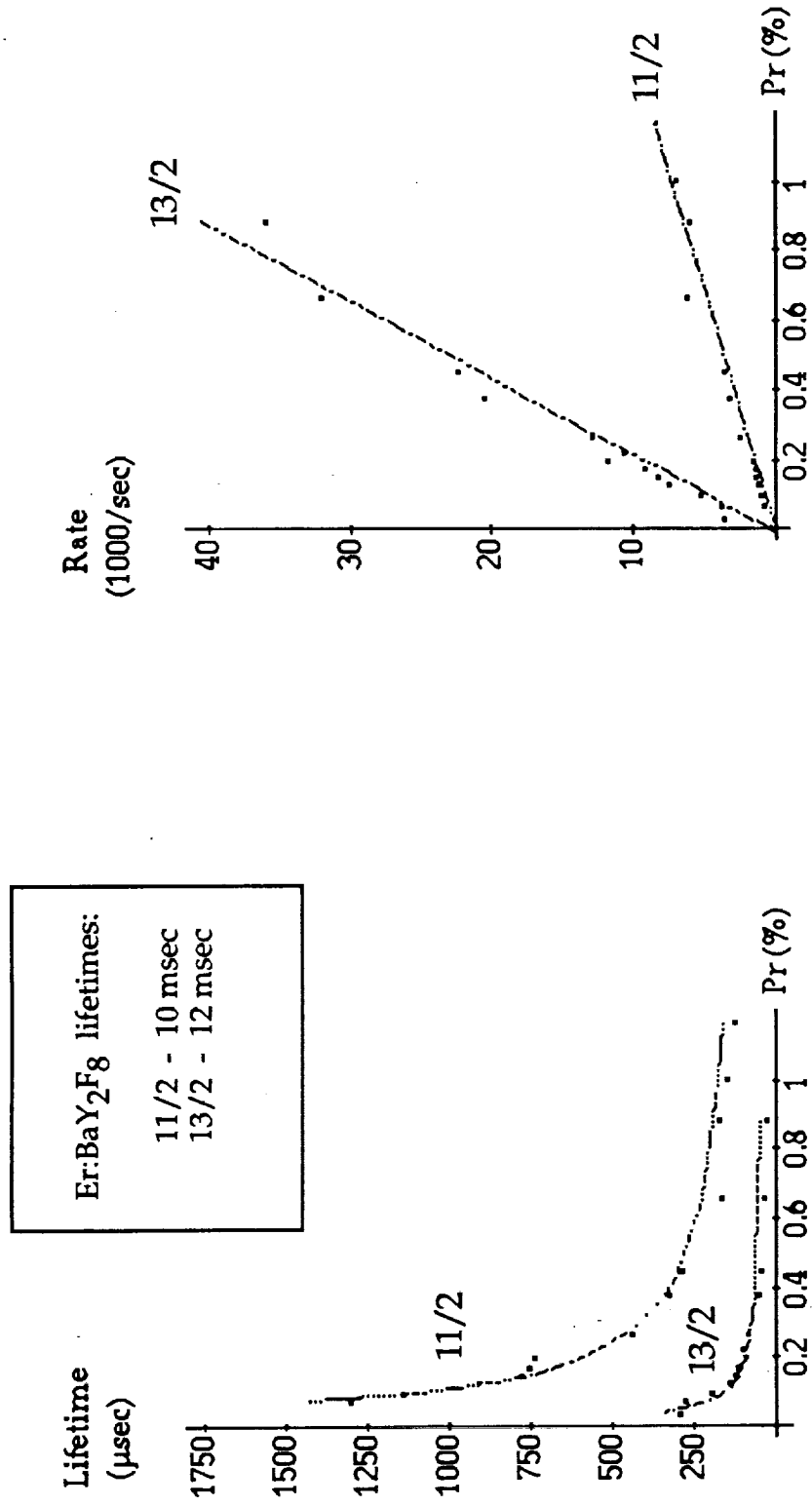
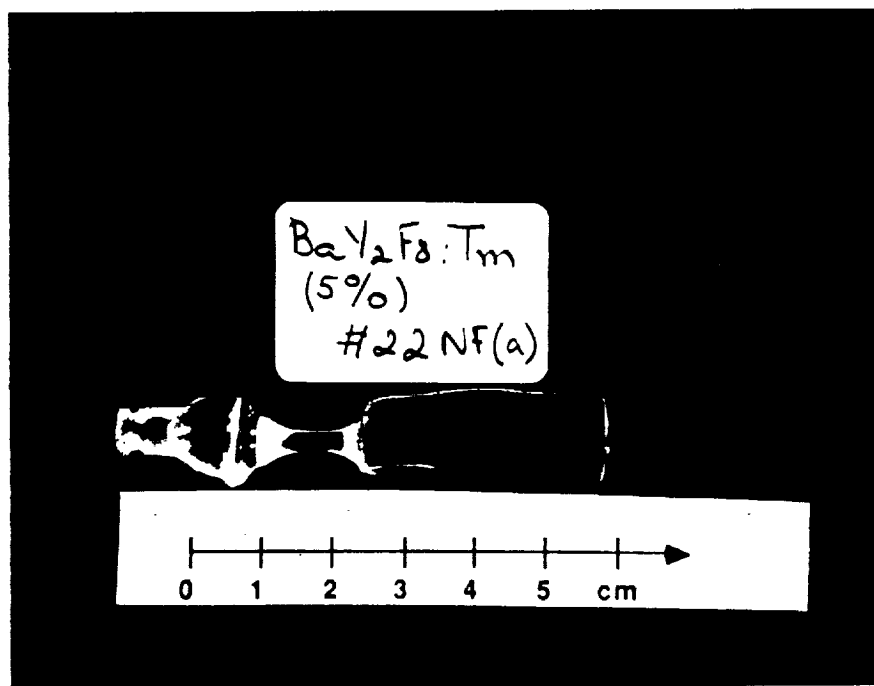Er:BaY$_2$F$_8$ lifetimes:

11/2 - 10 msec
13/2 - 12 msec

Figure 3. Quenching of Er by Pr

Fig4. Growth direction: "c"

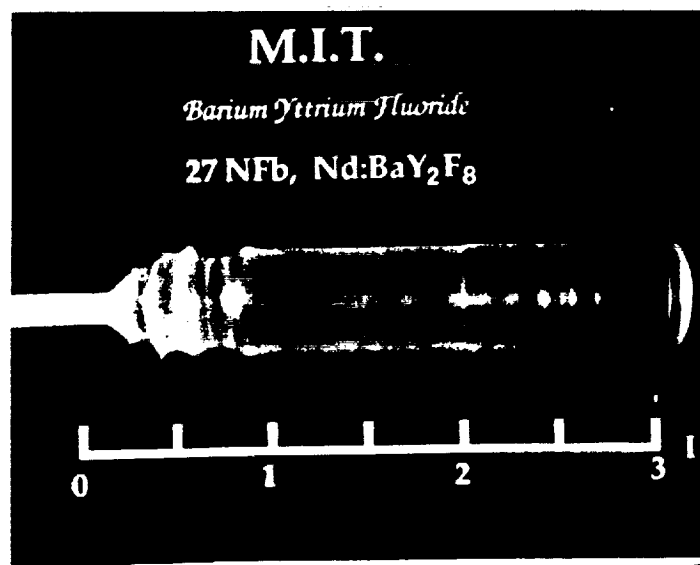Fig 5. Growth direction: "a"

M.I.T.

Barium Yttrium Fluoride

27 NFb, Nd:BaY$_2$F$_8$

Fig. 6. Growth direction: "a"