GROWTH AND CHARACTERIZATION OF MATERIALS FOR TUNABLE LASERS IN THE NEAR INFRARED SPECTRAL REGION

Principal Investigators
Richard C. Powell and Joel J. Martin

Department of Physics
Oklahoma State University
Stillwater, OK 74078-0444

NASA Research Grant NAG-1-694

Semi-annual Progress Report
1 February 1988 - 31 July 1988
INTRODUCTION

During the report period the work on this project proceeded in two areas. The first was the development of crystal growth procedures for rare earth doped LiYF₄ crystals. The procedures for growth and pre-growth treatment of the starting materials for undoped LiYF₄ crystals were established and good optical quality materials were grown. A significant amount of time was spent in trying to establish the optimum growth parameters for Yb³⁺-doped crystals. Unfortunately it has proven difficult to obtain large size boules of high optical quality crystals of LiYF₄ with doping concentrations of Yb³⁺ of several per cent. Because of these problems, we are changing our direction to attempt doping with other trivalent rare earth ions such as Ho, Er, and Tm.

The second research area was investigating the potential of LiNbO₃:Mg,Cr, and LiNbO₃:Mg,Cr,Yb as possible laser materials. The results obtained thus far are summarized in the following section.

The key personnel involved in the project during this time period were:

SPECTROSCOPY
Prof. R.C. Powell, P.I.
M.L. Kliewer, G.R.A.

CRYSTAL GROWTH
Prof. J.J. Martin, P.I.
D.L. Hart, G.R.A.

The major travel expense was for one of the principal investigators (J.J.M.) to visit NASA Langley Research Center to discuss this research project.
SPECTROSCOPIC STUDY OF LiNbO$_3$:Mg,Cr and LiNbO$_3$:Mg,Cr,Yb

LiNbO$_3$:Mg,$Cr^{3+}$ crystals were grown doped with a variety of rare earth ions. The rare earth ions under investigation are Eu, Tm, Ho, Nd, Er, and Yb. The first three materials have been sent to NASA for studies on the energy transfer from $Cr^{3+}$ to the rare earth ions. The two samples investigated here were of good optical quality and were grown by the Czochralski technique in the crystal growth facility at Oklahoma State University. The first was a single crystal of LiNbO$_3$ doped with 4.5% MgO and 0.05% Cr$_2$O$_3$. The concentration of $Cr^{3+}$ in the crystal was $3.6 \times 10^{19}$ cm$^{-3}$. The magnesium quenches the photorefractive effect that takes place in LiNbO$_3$ and also alleviates the crystal-cracking problem during growth.$^1$ The second sample consists of a single crystal of LiNbO$_3$ doped with 4.5% MgO, 0.05% Cr$_2$O$_3$, and 0.1% Yb$_2$O$_3$. The concentration of $Cr^{3+}$ was $9.06 \times 10^{18}$ cm$^{-3}$ and of $Yb^{3+}$ was $1.37 \times 10^{19}$ cm$^{-3}$.

There are many reasons that suggest that the $Cr^{3+}$ ions lie in the Nb sites of LiNbO$_3$.$^{10}$ Below the ferroelectric Curie temperature of 1190°C, LiNbO$_3$ is rhombohedral, belonging to the space group R3c at room temperature.$^2$ The Li$^+$ ion lies in the oxygen plane at the growth temperature and down to the Curie temperature, so the only octahedral site is the Nb site. Since the $Cr^{3+}$ ions prefer octahedral coordination the Nb sites are more probable.$^3$ On the basis of size ($Cr^{3+}$ radius = 0.63 A, Li$^+$ radius = 0.68, Nb$^{4+}$ radius = 0.67) and charge misfits, the $Cr^{3+}$ ion is as likely to enter the Li$^+$ sites as the Nb$^{4+}$ sites, but less likely to enter the vacancy sites. The electronegativity of
Cr\textsuperscript{3+} is 1.6, while that of Li\textsuperscript{+} and Nb\textsuperscript{4+} is 0.95 and 1.7, respectively, so on the basis of substitutional sites, Nb\textsuperscript{4+} is preferred. In light of the above discussion, the most probable site for the Cr\textsuperscript{3+}-ion impurity in LiNbO\textsubscript{3} is the Nb site. From electron-spin-resonance spectra, it is believed that the Yb\textsuperscript{3+} is probably substitutional on the Li site.

The unpolarized absorption spectra of LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+} and LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+},Yb\textsuperscript{3+} are taken on a Perkin-Elmer Spectrophotometer Model 330 and is shown as the solid lines in Figures 1 and 2, respectively. The energy assignments of Cr\textsuperscript{3+} and Yb\textsuperscript{3+} are given in Table 1. The absorption exhibits the characteristic transition from the \textsuperscript{4}A\textsubscript{2} level to the \textsuperscript{4}T\textsubscript{1} level peaked at 480 nm and the transition from the \textsuperscript{4}A\textsubscript{2} level to the \textsuperscript{4}T\textsubscript{2} level peaked at 650 nm of chromium. The transition from the \textsuperscript{2}F\textsubscript{7/2} ground state to the \textsuperscript{2}F\textsubscript{3/2} excited state of ytterbium is located at 925 nm.

The fluorescence spectra of LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+} and LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+},Yb\textsuperscript{3+} is obtained by exciting the chromium \textsuperscript{4}T\textsubscript{1} level with a Coumarin 500 dye that is pumped with a N\textsubscript{2} laser. Figure 1 shows the low temperature (12 K) and room temperature fluorescence of LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+}. The broadband emission that peaked at 925 nm is due to the transition from the \textsuperscript{4}T\textsubscript{2} to \textsuperscript{4}A\textsubscript{2} in chromium. Using the Tanabe-Sugano diagram for d\textsuperscript{3} ions, \textsuperscript{5} the crystal field splitting is determined to be 14942 cm\textsuperscript{-1}. This crystal field splitting is calculated using the Racah parameter value for B of 482 cm\textsuperscript{-1}. \textsuperscript{3} No "R" lines are seen in the room temperature luminescence because the probability of nonradiative decay from the \textsuperscript{2}E state is much greater than the probability of
radiative decay (approximately 10 orders of magnitude). This is because the $^4T_2$ level drops below the $^2E$ level and most of the excited state population relaxes to the lowest level.

A large Stoke's shift between the absorption and emission band is seen in these materials. The stimulated emission cross section for broadband materials with a large Stoke's shift is given by

$$\sigma_{21} = \frac{1}{4\pi^2 R \Delta \nu} \left( \frac{\lambda_{em}^3}{\lambda_{ab}} \right) \left[ g_u / (g_1 n_{ab} n_{em}) \right] \left( M_{ab} / M_{em} \right)^2 \times \left( \xi_{em} / \xi_{ab} \right)^2$$

where $\lambda_{em}$ is the wavelength of the peak of the emission band and $\lambda_{ab}$ is the wavelength of the peak of the absorption band, $\Delta \nu$ is the full width at half maximum of the absorption band, $n_{em}$ and $n_{ab}$ are the indices of refraction of the material at emission and absorption, respectively, $\tau_R$ is the radiative lifetime of the material, $g_u$ and $g_1$ are the degeneracies of the upper and lower levels of the transition, $\xi_{em}$ and $\xi_{ab}$ are the effective fields surrounding the ion in the host at the wavelengths of the emission and absorption transitions, and $M_{ab}$ and $M_{em}$ are the matrix elements of the absorption and emission transitions. For zero-phonon lines $\lambda_{ab} = \lambda_{em}$, and Eq. (1) becomes the familiar expression for the emission cross section. For the samples of interest, no zero-phonon lines are observed, the shapes of the absorption bands are distorted by the band edges of the host crystal, there are large Stokes' shifts, and the quantum efficiencies are not known. However, Eq. (1) still can be used to obtain an estimate for $\sigma_{21}$ by approximating the radiative lifetime by the measured low temperature fluorescence lifetime, approximating the half-
width of the absorption band with the measured halfwidth of the emission band, assuming that the effective fields, refractive indices, and matrix elements are the same for absorption and emission wavelengths, and assuming that the degeneracies of the upper and lower levels of the transition are equal. The emission cross sections for the chromium estimated from spectral parameters in this way is listed in Table 2.

The 1/e value of the fluorescence lifetime versus temperature of both LiNbO₃:MgO,Cr³⁺ and LiNbO₃:MgO,Cr³⁺,Yb³⁺ is shown in Figure 3. Below room temperature, the lifetime of chromium in LiNbO₃ is double exponential and this may be due to the Cr³⁺ ion occupying both the Li and the Nb sites in the host. When room temperature is reached, the fluorescence lifetime becomes single exponential. The 1/e value of the fluorescence lifetime is constant out to about 100 K with an exponential decrease for temperature up to about 300 K. This rapid decrease in lifetime is attributed to nonradiative processes. A simple two level model described by the equation

\[ \frac{1}{\tau} = \frac{1}{\tau_L} + C \exp\left(-\frac{\Delta E}{kT}\right) \]

(2)

where \( \tau \) is the fluorescence lifetime, \( \tau_L \) is the lifetime at low temperatures, and \( \Delta E \) is the energy difference between the \( 4T_2 \) level and the \( 4A_2 \) level is used to describe the process. A \( \Delta E \) of 618 cm⁻¹ is found for both LiNbO₃:MgO,Cr³⁺ and LiNbO₃:MgO,Cr³⁺,Yb³⁺ indicating that the Yb³⁺ ion does not alter the energy difference of the \( 4T_2 \) to the \( 4A_2 \). The fit to Eq. (2) is shown as the solid line in Figure 3.

If the pump power is increased while monitoring the fluorescence lifetime, an effective "lifetime shortening" of the
fluorescence is seen. This lifetime shortening takes place due to either stimulated emission or excited state absorption. The lifetime shortening occurs at a definite threshold value of the pump pulse energy referred to as \( E_{\text{th}} \).\(^{14}\) For good vibronic laser materials where the absorption is negligible in the spectral region of the fluorescence emission, if the lifetime shortening takes place due to stimulated emission then the population of the upper state at threshold is\(^{14}\)

\[
(N_2)_{\text{th}} = \frac{E_{\text{th}}}{h\nu}
\]  

(3)

where \( \nu \) is the frequency of the pump pulse.

With the stimulated emission cross-section obtained from spectral parameters given from Eq. (1) and the population inversion at threshold from Eq. (3), the peak gain of the material is given by\(^6\)

\[
\gamma = \sigma_{21} (N_2)_{\text{th}}.
\]  

(4)

Lifetime shortening is seen in \( \text{LiNbO}_3: \text{MgO}, \text{Cr}^{3+} \) but the other material of interest, \( \text{LiNbO}_3: \text{MgO}, \text{Cr}^{3+}, \text{Yb}^{3+} \), is still under investigation. Figure 4 shows the definite threshold from spontaneous to stimulated processes in \( \text{LiNbO}_3: \text{MgO}, \text{Cr}^{3+} \). These stimulated processes can be either stimulated emission or excited state absorption. Assuming that this process is stimulated emission and using the experimentally determined value for \( E_{\text{th}} \), the population inversion at threshold can be determined from Eq (3). Using Eqs. (1) and (4), the peak gain is calculated and these values are given in Table 2.

An attempt was made to lase \( \text{LiNbO}_3: \text{MgO}, \text{Cr}^{3+} \) by placing it into a cavity with a 97% output coupler and side pumping the
system with the second harmonic of a nanosecond Nd:YAG laser. Fluences of 2.5 J/cm$^2$ were obtained with surface damage occurring at fluences greater than 650 mJ/cm$^2$. Lasing of the material was not achieved because the material is not highly absorptive at 532 nm and damage to the crystal occurred around the energy density needed for gain to be seen. The samples were AR coated and again placed in a cavity and side-­pumped with an alexandrite laser operating at 735 nm. Thermal cracking in each sample is observed before lasing can be achieved. Different designs for heat sinks are presently being investigated to alleviate this problem.

Time-resolved site-­selection spectroscopy (TRSSS) measurements are used to characterize the properties of short range energy transfer from the Cr$^{3+}$ ions to the Yb$^{3+}$ ions in LiNbO$_3$:MgO,Cr$^{3+}$,Yb$^{3+}$. The absorption of Yb$^{3+}$ occurs in the emission of Cr$^{3+}$ as shown in Figs. 2 and 5 indicating a direct absorption of the Cr$^{3+}$ emission by the Yb$^{3+}$ ions and making nonradiative energy transfer from Cr$^{3+}$ to Yb$^{3+}$ probable. A nitrogen laser pumped dye laser using Coumarin 500 dye is used to selectively excite the Cr$^{3+}$ ions. The fluorescence is directed through a one meter Spex monochromator and detected with an RCA 7102 photomultiplier tube. A boxcar integrator is used and the results are printed onto a chart recorder.

Energy transfer occurs from Cr$^{3+}$ to Yb$^{3+}$ and this is seen in the absorption and fluorescence of Yb$^{3+}$ in the Cr$^{3+}$ emission band for both short and long times as shown in Fig. 2. At short times after excitation of the $^4T_2$ band of Cr$^{3+}$, the absorption of Yb$^{3+}$ is seen in the Cr$^{3+}$ band, however, at longer times when the lifetime of the chromium ion is relatively short, the Yb$^{3+}$
emission becomes apparent.

It is important to determine the type and strength of the energy transfer mechanism and whether the energy transfer is a resonant or phonon-assisted process. The primary parameter of concern is the energy transfer rate $W_{sa}$.

The lifetime of the fluorescence versus temperature is measured for LiNbO$_3$:MgO,Cr$^{3+}$,Yb$^{3+}$ and LiNbO$_3$:MgO,Cr$^{3+}$ to determine if the energy transfer rate is temperature dependent. Because the lifetime of Cr$^{3+}$ in LiNbO$_3$ is multi-exponential only the $1/e$ value is shown in Fig. 3. The effective lifetime of LiNbO$_3$:MgO,Cr$^{3+}$ can be described as

$$\frac{1}{\tau}_{\text{eff}} = \frac{1}{\tau}_f$$

and the effective lifetime of LiNbO$_3$:MgO,Cr$^{3+}$,Yb$^{3+}$ can be described as

$$\frac{1}{\tau}''_{\text{eff}} = \frac{1}{\tau}''_f + W_{sa}$$

where $\frac{1}{\tau}_f$ is the fluorescence lifetime which consists of a radiative and a nonradiative part. If the chromium ion is in the excited state, then the transfer of energy from the chromium to the ytterbium is an addition decay mechanism called the average energy transfer rate given as $W_{sa}$ in Eq (6). Assuming that the presence of the ytterbium does not introduce structural changes in the crystal and that

$$\frac{1}{\tau}_f = \frac{1}{\tau}''_f,$$

then the average energy transfer rate is given by

$$(W_{sa})_{\text{avg}} = \frac{1}{\tau}''_{\text{eff}} - \frac{1}{\tau}_{\text{eff}}.$$ 

By taking the measured fluorescence lifetime as the effective lifetime, the average energy transfer rate is determined and the
results shown in Fig. 6. The average energy transfer rate increases dramatically at 200 K indicating that this energy transfer process is a phonon-assisted process.

The energy transfer rate can also be approximated by

\[(\kappa_{sa})_{av} = \frac{1}{\tau_{cr}} (R_0/R)^6 \]  

where \( R \) is the distance from the chromium ion to the ytterbium ion in the crystal and \( \tau_{cr} \) is the lifetime of the chromium ion. The value of \( R \) is determined to be 0.162 nm and using Eq. (9), the critical interaction distance, \( R_0 \), at which the energy transfer rate equals the intrinsic decay rate can be calculated and these values are given in Table 3.

The critical interaction distance can also be determined from spectral parameters for a dipole-dipole interaction mechanism using\(^8,9\)

\[ R_0 = \left[ \frac{3h^4 c^4}{4\pi n^4} Q_A \left( \int \frac{f_S(E) F_A(E)}{E^4} dE \right) \right]^{1/6}. \]  

\( n \) is the index of refraction of the material, \( f_S(E) \) is the normalized emission lineshape, \( F_A(E) \) is the normalized absorption lineshape, and \( Q_A = \int \sigma(v) dv \) is the integrated absorption cross section. The room temperature value for \( R_0 \) obtained from spectral parameters is 1.16 nm.

The time evolution of the fluorescence of the chromium and the absorption/fluorescence of the \( \text{Yb}^{3+} \) in \( \text{LiNbO}_3: \text{MgO}, \text{Cr}^{3+}, \text{Yb}^{3+} \) at different times is also investigated. There is a change in the ratios of the integrated fluorescence intensities of the chromium sites (sensitizers) to that of the Ytterbium (activators) sites that takes place. The values of the integrated fluorescence intensities are listed in Table 4. There
is an initial buildup of chromium along with absorption of the Ytterbium in the chromium band. As the intensity of the chromium emission decreases, the ytterbium fluorescence intensity increases. At long times only ytterbium emission is seen, implying there exists no back transfer.

The time evolution of the ratios can be modeled using a phenomenological rate parameter model illustrated in Figure 5. The sensitizer ions are those in the site that are preferentially excited by the laser at a rate $W_s$, whereas the activators are ions at sites that receive energy through energy transfer. $n_a$ and $n_s$ are the concentrations of the ions in the excited states, $W_{sa}$ is the rate of energy transfer from sensitizer to activator, and $\beta_s$ and $\beta_a$ are the fluorescence decay rates associated with each type of site. Thus, the rate equations describing the time evolution of the populations of the excited states can be written as

$$n_s = W_s - \beta_s n_s - W_{sa} n_s$$

$$n_a = -\beta_a n_a + W_{sa} n_s$$

The equations can be solved assuming a delta-function excitation pulse, negligible back-transfer, and an explicit time dependence for the energy transfer rate. The best fits to the data for both low and high temperatures were obtained with an energy transfer rate which varies as $t^{-1/2}$ indicating that a dipole-dipole interaction may take place. The solutions to Equations (11) and (12) are given by

$$n_s(t) = n_s(0) \exp[-\beta_s t - 2\Omega t^{1/2}]$$

$$n_a(t) = n_s(0) (\exp[-\beta_s t] - \exp[-\beta_s t - 2\Omega t^{1/2}]) + n_a(0) \exp[-\beta_a t]$$

where the time dependence of the energy transfer rate is written
explicitly as \( W_{sa} = \Omega t^{-1/2} \). The ratio of the integrated fluorescence intensities is proportional to the rate of the excited state populations and can be written directly as

\[
\frac{I_a(t)}{I_s(t)} = \left( \frac{\beta_a \gamma}{\beta_s \gamma} \right) \left[ \left( \frac{I_a(0)}{I_s(0)} \right) \left( \frac{\beta_s \gamma}{\beta_a \gamma} \right) + 1 \right] \times \exp \left( 2\Omega t^{1/2} \right) - 1 \tag{15}
\]

where \( \beta_a \gamma \) and \( \beta_s \gamma \) are the radiative decay rates associated with the activator and sensitizer sites, respectively. As mentioned earlier, part of the transfer of energy from the Cr\(^{3+}\) to the Yb\(^{3+}\) is radiative and part of the energy transfer is nonradiative. Eq. 15 applies only to nonradiative energy transfer so radiative energy transfer must be considered in order to be able to fit Eq. 15 to experimental data. At very short times when the fluorescence of the chromium is at a maximum, it is assumed that the amount of radiative transfer is at a maximum. The fraction \( f \) of radiative energy transfer can be calculated by dividing the integrated intensity of the absorption of Yb\(^{3+}\) in the fluorescence of LiNbO\(_3\):MgO,Cr\(^{3+}\) by the integrated intensity of the fluorescence of LiNbO\(_3\):MgO,Cr\(^{3+}\). The correction for the ratio of integrated intensities when considering both radiative and nonradiative energy transfer is \((1-f)\) and Eq 15 becomes

\[
\left[ \frac{I_a(t)}{I_s(t)} \right] (1-f) = \left( \frac{\beta_a \gamma}{\beta_s \gamma} \right) \left[ \left( \frac{I_a(0)}{I_s(0)} \right) \left( \frac{\beta_s \gamma}{\beta_a \gamma} \right) + 1 \right] \times \exp \left( 2\Omega t^{1/2} \right) - 1 \tag{16}
\]

The solid and broken lines in Figure 7 represent the best fits of Equation (16) to the experimental data. Both \( I_a(0)/I_s(0) \) and \( \Omega \) are treated as adjustable parameters. The values for these parameters and for the fraction of radiative energy transfer are listed in Table 5.
It is possible to use the Forster-Dexter expression for an electric dipole-dipole transfer rate and the rate equation model to find the value of the critical interaction distance, $R_0$. This expression is given by

$$R_0 = \left( \frac{\Omega_D}{N_a} \right)^{1/2} \left[ \frac{(4/3) \pi^{3/2}}{\Omega_s} \right]^{-1/3} \Omega_s^{-1/2}$$

where $\Omega_D/N_a = \Omega_s^{-1/2}$.

$N_a$ is the total concentration of activators and $\tau_s$ is the lifetime of the sensitizer without the presence of activators. The values for $R_0$ at different temperatures is given in Table 5.

From the initial spectroscopy, LiNbO$_3$:MgO, Cr$_{3+}$ appears to be a promising tunable laser material. The broad absorption of the Cr$_{3+}$ ion makes flash lamp pumping possible and the broad fluorescence band peaked at 925 nm allows the possibility of tunability of a wide range in the near IR. Thermal effects cause the material to crack at room temperature making the cooling of this material imperative if it is to operate as a laser material at room temperature. Adequate cooling of the material is needed and operating at 77 K will increase the quantum efficiency making it possible for this material to work as a laser at low temperatures.

The energy transfer mechanisms between Cr$_{3+}$ and Yb$_{3+}$ in LiNbO$_3$:MgO, Cr$_{3+}$, Yb$_{3+}$ are studied above. Five to twenty percent of the energy transfer is radiative due to the absorption of the Yb$_{3+}$ ion lying at the peak of the Cr$_{3+}$ emission. The critical interaction distance ranges from 1.1 to 2.6 nm.
<table>
<thead>
<tr>
<th>Cr(^{3+})</th>
<th>O(_h)-Cubic Assignment</th>
<th>Experimental Energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{A}_2)</td>
<td>(0)</td>
<td></td>
</tr>
<tr>
<td>(2\text{E})</td>
<td>(13888)</td>
<td></td>
</tr>
<tr>
<td>(2\text{T}_1)</td>
<td>(14705)</td>
<td></td>
</tr>
<tr>
<td>(2\text{T}_2)</td>
<td>(15385)</td>
<td></td>
</tr>
<tr>
<td>(4\text{T}_1)</td>
<td>(20833)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yb(^{3+})</th>
<th>(2\text{F}_{7/2})</th>
<th>(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2\text{F}_{3/2})</td>
<td>(10811)</td>
</tr>
</tbody>
</table>
**Table 2. SAMPLE PARAMETERS**

<table>
<thead>
<tr>
<th></th>
<th>LiNbO$_3$:MgO, Cr$^{3+}$</th>
<th>LiNbO$_3$:MgO, Cr$^{3+}$, Yb$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{Cr}$ (cm$^{-3}$)</td>
<td>$3.6 \times 10^{19}$</td>
<td>$9.0 \times 10^{18}$</td>
</tr>
<tr>
<td>$N_{Yb}$ (cm$^{-3}$)</td>
<td>$1.4 \times 10^{-19}$</td>
<td>$1.4 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\sigma_{21}$ of Cr$^{3+}$ (cm$^2$)</td>
<td>$1.4 \times 10^{-19}$</td>
<td>$1.4 \times 10^{-19}$</td>
</tr>
<tr>
<td>$E_{th}$ (mJ)</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>$(N_2)_th$ (cm$^{-3}$)</td>
<td>$3.4 \times 10^{18}$</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ (cm$^{-1}$)</td>
<td>0.478</td>
<td></td>
</tr>
<tr>
<td>T(K)</td>
<td>$\tau'$ (usec)</td>
<td>$\tau$ (usec)</td>
</tr>
<tr>
<td>------</td>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>12</td>
<td>7.02</td>
<td>9.06</td>
</tr>
<tr>
<td>30</td>
<td>6.55</td>
<td>9.31</td>
</tr>
<tr>
<td>40</td>
<td>6.68</td>
<td>8.90</td>
</tr>
<tr>
<td>50</td>
<td>6.35</td>
<td>9.04</td>
</tr>
<tr>
<td>75</td>
<td>6.33</td>
<td>9.11</td>
</tr>
<tr>
<td>125</td>
<td>5.73</td>
<td>7.96</td>
</tr>
<tr>
<td>150</td>
<td>5.39</td>
<td>7.58</td>
</tr>
<tr>
<td>200</td>
<td>3.62</td>
<td>4.78</td>
</tr>
<tr>
<td>250</td>
<td>1.81</td>
<td>2.60</td>
</tr>
<tr>
<td>295</td>
<td>1.06</td>
<td>1.78</td>
</tr>
</tbody>
</table>
Table 4. **TIME EVOLUTION OF THE INTEGRATED AREAS OF THE ACTIVATOR AND SENSITIZER FLUORESCENCE VERSUS TEMPERATURE**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{yb}/I_{cr}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.0</td>
<td>0.0</td>
<td>2.87</td>
<td>9.70</td>
<td></td>
<td>24.56</td>
</tr>
<tr>
<td>50</td>
<td>0.0</td>
<td>0.0</td>
<td>1.53</td>
<td>4.06</td>
<td>9.97</td>
<td>----</td>
</tr>
<tr>
<td>100</td>
<td>0.0</td>
<td>0.0</td>
<td>1.08</td>
<td>3.56</td>
<td></td>
<td>----</td>
</tr>
<tr>
<td>200</td>
<td>0.0</td>
<td>0.0</td>
<td>3.06</td>
<td></td>
<td></td>
<td>----</td>
</tr>
</tbody>
</table>
TABLE 5. ADJUSTABLE PARAMETERS USED IN FITTING OF SPECTRAL
ENERGY TRANSFER RATE EQUATION MODEL

<table>
<thead>
<tr>
<th>T(K)</th>
<th>f</th>
<th>I_a(0)/I_s(0)</th>
<th>Ω(s^{-1/2})</th>
<th>R_0 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.185</td>
<td>391.4</td>
<td>173</td>
<td>1.72</td>
</tr>
<tr>
<td>50</td>
<td>0.056</td>
<td>110.0</td>
<td>272</td>
<td>1.98</td>
</tr>
<tr>
<td>100</td>
<td>0.067</td>
<td>227.3</td>
<td>325</td>
<td>2.09</td>
</tr>
<tr>
<td>200</td>
<td>0.042</td>
<td>7.3</td>
<td>496</td>
<td>2.18</td>
</tr>
<tr>
<td>295</td>
<td>0.060</td>
<td>3.3</td>
<td>1371</td>
<td>2.60</td>
</tr>
</tbody>
</table>
Fig. 1. Absorption (solid line) and Fluorescence (broken line) of LiNbO\textsubscript{3}:Mg,Cr.

Fig. 2. Absorption (solid line) and fluorescence (broken and dashed lines) of LiNbO\textsubscript{3}:Mg,Cr,Yb. The broken line is the fluorescence 1 µs after the pump pulse and the dashed line is the fluorescence 100 µs after the pump pulse. The fluorescence shown was taken at 12 K.

Fig. 3. 1/e value of the fluorescence decay as a function of temperature. The open circles are the lifetimes of LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+} and the open triangles are the lifetimes of LiNbO\textsubscript{3}:MgO,Cr\textsuperscript{3+},Yb\textsuperscript{3+}. The solid lines are fits to the temperature dependence of the lifetime.

Fig. 4. Lifetime shortening of LiNbO\textsubscript{3}:Mg,Cr

Fig. 5. Energy level diagram of the Cr\textsuperscript{3+} and the Yb\textsuperscript{3+}. The solid line is the absorption of the chromium and the broken line is the emission of the chromium. The rate parameter model for the interpretation of spectral energy transfer data is also shown.

Fig. 6. (\textit{W}_\text{sa})_{\text{avg}} versus T
REFERENCES


\[ ^2T_2 \quad ^4T_2 \quad ^4T_2 \]

\[ W_s \quad \beta_s \]

\[ ^4A_2 \quad \text{Cr}^{3+} \]

\[ \beta_a \]

\[ ^2F_{3/2} \quad ^7F_{7/2} \quad \text{Yb}^{3+} \]