Spectroscopic and laser properties of Cr$^{3+}$ : Yb$^{3+}$ : Er$^{3+}$ : fluoride phosphate glass

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Sensitization of the fluorescence of Er$^{3+}$ in fluoride phosphate glass containing up to 20 mol % phosphates by codoping with Cr$^{3+}$ and Yb$^{3+}$ is shown. The low order of ligand field strength for Cr$^{3+}$ ($Dq/B = 2.04$) results in broad Cr$^{3+}$ fluorescence overlapping the Yb$^{3+}$ absorption. The electronic energy transfer efficiency approaches 100%. Deviations of donor decay from the Förster law are interpreted in terms of the inhomogeneously acceptor distribution. The electronic energy transfer efficiency of Yb$^{3+}$ → Er$^{3+}$ reaches a maximum value of 75% for glasses containing 20 mol % phosphates. The transfer is shown to be migrationally accelerated by means of GAF–LAF–FB theory. From Judd–Ofelt parameters a stimulated emission cross-section for the transition $^4I_{13/2} \rightarrow ^4I_{15/2}$ of Er$^{3+}$ of $6.2 \times 10^{-20}$ cm$^2$ is derived. The c.w. laser action of Er$^{3+}$ by Cr$^{3+}$ excitation and double-step energy transfer is shown. The output is tuned continuously from 1536 to 1596 nm. Flashlamp pumping is also shown.

1. Introduction
Erbium glass lasers have been known since the early days of solid-state laser research. Laser action of trivalent erbium in silicate glasses was first obtained by Snitzer and Woodcock [1]. The lasing wavelength of 1540 nm raised strong interest for reasons of eye safety and easy detection. The disadvantage of only some weak absorption bands of Er$^{3+}$ in the visible range led to the sensitization of fluorescence by codoping with trivalent ytterbium [1, 2]. Much work was done by Soviet scientists [3–7]. Further sensitization with Nd$^{3+}$ suffered from the disadvantage of back-transfer from Er$^{3+}$ to Nd$^{3+}$ [5]. Another possibility for the enhancement of the efficiency of this kind of laser is the use of transition-metal ions as additional sensitizers, for instance Cr$^{3+}$ [8–10]. A record high lamp pump efficiency of 1.7% with a threshold of 5 J was reported by Gapontsev et al. [11] in phosphate glass.

The c.w. laser action of Er$^{3+}$ in silica fibres via argon laser pumping was achieved by Mears et al. [12]. The output was tunable from 1528 to 1555 nm.
The laser action of Er$^{3+}$ in fluoride phosphate glass under krypton laser pumping via the energy transfer steps Cr$^{3+}$ $\rightarrow$ Yb$^{3+}$ and Yb$^{3+}$ $\rightarrow$ Er$^{3+}$ (see Fig. 1) was reported by Heumann et al. [13, 14]. Tuning was shown between 1536 and 1596 nm.

2. Characterization of host glasses

Fluorophosphate glasses have been used as host materials for Er$^{3+}$ several times [15]. In our case we used fluoride phosphate glasses with various phosphate contents:

- fluorides (AlF$_3$, MgF$_2$, CaF$_2$, SrF$_2$): 100 to 80 mol %
- phosphates (Sr(PO$_3$)$_2$, Ba(PO$_3$)$_2$): 0 to 20 mol %

The following abbreviations are used: Sx or Bx means a content of x mol % Sr(PO$_3$)$_2$ or Ba(PO$_3$)$_2$, respectively, and C, Y and E denote Cr$^{3+}$, Yb$^{3+}$ and Er$^{3+}$, respectively.

The homogenized compounds were melted in a platinum crucible at 1000 to 1200°C. After a short refinement and homogenization the melt was cast into preheated graphite.
Properties of Cr$^{3+}$ : Yb$^{3+}$ : Er$^{3+}$ : fluoride phosphate glass

moulds and cooled to room temperature at 2 to 3 K min$^{-1}$ [16]. Some characteristic parameters are the glass transition temperature $T_g = 470^\circ$C, crystallization temperature $T_c = 580^\circ$C, bulk index of refraction $n_b = 1.51$, Abbe number $v = 80$, gap of infrared (IR) absorption $\geq 4 \mu m$ and density $\rho = 3.55 g cm^{-3}$.

3. Experimental set-up
Absorption spectra were recorded in the visible region with an MV 40 absorption spectrometer and in the infrared (IR) region with an NIR 65 (both Carl Zeiss Jena, GDR). Fluorescence spectra were registered with an OVA 284 multichannel analyser (Academy of Sciences, Berlin, GDR) or with an SPM 2 monochromator (Carl Zeiss Jena, GDR) in combination with a germanium diode in the visible and IR region, respectively. Time-resolved spectra were recorded with a BCI 280 boxcar integrator (Academy of Sciences, Berlin, GDR).

Spectra were excited with a krypton ion laser (647.1 and 676.4 nm) or with the radiation of a frequency-doubled c.w. Q-switched Nd: YAG laser. Excitation and detection were made perpendicular to prevent reabsorption effects. Time-dependent spectra were transferred to a microcomputer and handled with appropriate mathematical fitting procedures.

4. Spectroscopic properties of Cr$^{3+}$ in fluoride phosphate glass
The spectroscopic properties of the transition metal ion Cr$^{3+}$ are influenced strongly by the surroundings. This originates from the interaction of the neighbouring ions with the three outer electrons of Cr$^{3+}$ (electron configuration (Ar)3d$^3$) in an unfilled shell. Here the ligands are F$^-$ and O$^{2-}$ ions from the fluorides and phosphates of the bulk material. A valid description of this kind of interaction is possible on the basis of ligand field theory [17].

Normally electric dipole transitions within the d-shell are parity-forbidden. This selection rule is broken by the admixture of appropriate wavefunctions via non-centrosymmetric parts of the crystal field or due to non-centrosymmetric phonons.

Much work has been done on the spectroscopy of Cr$^{3+}$ in glasses, for instance by Lempicki and co-workers [18, 19]. A widely used method for the description of the absorption spectra of co-ordinated transition-metal ions was given by Tanabe and Sugano [20]. The position of the energy levels is described by three parameters. The parameter $D_q$ is a measure of the strength of the ligand field, and $B$ and $C$ characterize the electron interaction. From Henry et al. [21] it follows that

$$10D_q = E(^4T_2)$$

$$D_q/B = \frac{15(x - 8)}{x^2 - 10x}$$

with

$$x = \frac{E(^4T_1) - E(^4T_2)}{D_q}$$

The absorption spectra of fluoride phosphate glass S20 C2 ($n_{cr}^{3+} = 2 \times 10^{19} cm^{-3}$) is shown in Fig. 2. Three broad bands can be seen, corresponding to the transitions $^4A_2 \rightarrow ^4T_2$ (15 400 cm$^{-1}$), $^4A_2 \rightarrow ^4T_1 (t_{2g}^2e_{g}^0)$ (22 525 cm$^{-1}$) and $^4A_2 \rightarrow ^4T_1 (t_{2g}^0e_{g}^2)$ (34 200 cm$^{-1}$).

The band near 15 400 cm$^{-1}$ shows sharp features at 14 800 and 15 700 cm$^{-1}$ originating from the spin-forbidden transitions $^4A_2 \rightarrow ^2E$ and $^4A_2 \rightarrow ^2T_1$, respectively. The decrease of
the absorption coefficient in the vicinity of these transitions can be understood as Fano-type antiresonances [18, 22, 23]. A detailed description of Fano antiresonances in these kind of glasses is given in [24].

From Fig. 2 one can derive the parameters $Dq$ and $B$ with the help of Equations 1 to 3. They are listed together with the position of the $2E$ level and the value of $C$ in Table I. It should be remarked that the position of the $2E$ level is not equal to the position of the notch in the absorption spectrum, because of the blue shift due to coupling of $4T_2$ and $2E$ [18]. Because of the evidence of inhomogeneous broadening in glasses, one can mostly find some $Cr^{3+}$ ions with $2E$ as the lowest excited level (high-field sites). They give rise to fluorescence $3E \rightarrow 4A_2$ (R-line). The parameter $C$ was found by diagonalizing the energy matrix of $3E$ [20] and adjusting with regard to the R-line position. Using the parameters of Table I, a Tanabe--Sugano diagram was calculated with the help of the energy matrices of [20]. This is shown in Fig. 3.

From Fig. 3 one can ascribe the asymmetry of the absorption band $^4A_2 \rightarrow ^4T_1 (t_{2g}e_g^1)$ (Fig. 2) to an antiresonance of this level with $^2T_2$.

The time behaviour of the $Cr^{3+}$ fluorescence decay shows a complex dependence on the host-glass composition, registration wavelength and temperature. In addition, the decay is non-exponential. The best fit of the decay curves is possible under the assumption of a two-exponential decay model. This model is probably due to the special type of glasses which should allow $Cr^{3+}$ ions to be sometimes in more-fluoride- and at other times in more-oxygen-like surroundings. For glass type S20 C2 at 800 nm and room temperature...
the best fit is realized with time constants of 8 and 30 \( \mu s \). For a more detailed discussion, see [24].

5. Energy-transfer step \( \text{Cr}^{3+} \rightarrow \text{Yb}^{3+} \)

A criterion for strong electronic energy transfer is a good spectral overlap of donor fluorescence and acceptor absorption. Electronic energy transfer from \( \text{Cr}^{3+} \) to \( \text{Yb}^{3+} \) in most crystals is unlikely because of the relatively strong energy gap between \( \text{Cr}^{3+} \) fluorescence and \( \text{Yb}^{3+} \) absorption [25]. Because of the low crystal field, this transfer step should have a higher probability in glasses. The spectral overlap of \( \text{Cr}^{3+} \) fluorescence and \( \text{Yb}^{3+} \) absorption is shown in Fig. 4. The decrease of static \( \text{Cr}^{3+} \) fluorescence with increasing content of \( \text{Yb}^{3+} \) is shown in Fig. 5. Even with small amounts of \( \text{Yb}^{3+} \) \( (7 \times 10^{19} \text{cm}^{-3}) \) the \( \text{Cr}^{3+} \) fluorescence decreases strongly and nearly vanishes at \( \text{Yb}^{3+} \) concentrations of \( 6 \times 10^{20} \text{cm}^{-3} \). The transfer rate approaches 100%.

Because of the homogeneity of glasses and because of the order of \( \text{Yb}^{3+} \) concentration in comparison with \( \text{Cr}^{3+} \), one would assume the validity of the well-known Förster law for donor decay [26, 27]:

\[
I(t) = I_0(t = 0) \exp \left( -t/\tau_D - kt^{1/2} \right) \quad (4)
\]

where \( \tau_D \) is the intrinsic donor lifetime and

\[
k = \frac{3}{4} \pi^{3/2} N_A R_0^3 \tau_D^{-1/2} \quad (5)
\]
Figure 4 Spectral overlap of (1) Cr$^{3+}$ emission and (2) Yb$^{3+}$ absorption in glass type S10.

Figure 5 Decrease of Cr$^{3+}$ fluorescence intensity with increasing concentration of Yb$^{3+}$ for glass type S15. The Cr$^{3+}$ concentration is $2 \times 10^{19}$ cm$^{-3}$. The concentration of Yb$^{3+}$ in units of $10^{21}$ cm$^{-3}$ is (1) 1.0, (2) 0.07, (3) 0.15, (4) 0.3, (5) 0.6, (6) 0.9 and (7) 1.2. Spectra are normalized to pure Cr$^{3+}$ fluorescence.

Here $N_A$ is the acceptor concentration and $R_0$ is the Förster radius. Often the micro-parameter of transfer $c_{DA}$ is introduced:

$$c_{DA} = \frac{R_0^6}{\kappa_D}$$  \hspace{1cm} (6)

According to the two-centre model one should assume a two-fold Förster function to fit the Cr$^{3+}$ decay. In spite of four fitting parameters this led to a larger root mean square error.
Properties of Cr$^{3+}$ : Yb$^{3+}$ : Er$^{3+}$ : fluoride phosphate glass

Figure 6 Dependence of Förster parameter $k$ (Equations 4 and 5) on the acceptor concentration for the energy transfer step Cr$^{3+} \rightarrow$ Yb$^{3+}$ for glasses with different phosphate contents. (---) S10, (---) S15 and (-----) S20. $n_{D3+} = 2 \times 10^{19}$cm$^{-3}$.

TABLE II Microparameter $c_{DA}$ and Förster radii $R_0$ for the energy transfer step Cr$^{3+} \rightarrow$ Yb$^{3+}$ for glasses containing different concentrations of phosphates

<table>
<thead>
<tr>
<th>Type of glass</th>
<th>$c_{DA}$ (10$^{-38}$cm$^6$s$^{-1}$)</th>
<th>$R_0$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10</td>
<td>1.3</td>
<td>0.81</td>
</tr>
<tr>
<td>S15 1st part</td>
<td>10.4</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>2nd part</td>
<td></td>
</tr>
<tr>
<td>S20</td>
<td>2.5</td>
<td>0.93</td>
</tr>
</tbody>
</table>

than the use of a single $\tau_D$. This shows that the transfer occurs mainly from this Cr$^{3+}$ centres which obey the larger decay constant. The best fit was obtained with a single Förster function with a $\tau_D$ of 25 $\mu$s.

The dependence of the Förster parameter $k$ on the acceptor concentration is shown in Fig. 6. The dependence is not linear, in contrast to Equation 5. Two linear functions were fitted. The related $c_{DA}$s and $R_0$s are given in Table II.
Inhomogeneous acceptor distribution density \( w(r) \) for the transfer step \( \text{Cr}^{3+} \rightarrow \text{Yb}^{3+} \).

The Förster radius can also be obtained from the overlap spectrum (Fig. 4) [26, 27, 28]:

\[
\begin{align*}
R_0^0 &= \frac{9000 \ln(10) \eta D}{128 \pi^2 n^4 N_A} \int_0^{\infty} F_D(\tilde{\nu}) e_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\nu^2} \\
&= \frac{9000 \ln(10) \eta D}{128 \pi^2 n^4 N_A} \int_0^{\infty} F_D(\nu) e_A(\nu) \frac{d\nu}{\nu^2} 
\end{align*}
\]

where \( n \) is the refractive index, \( \eta_D \) the quantum efficiency of the donor, \( N_A \) is Avogadro's number, \( F_D \) the normalized donor emission spectrum and \( e_A \) the acceptor extinction.

With a quantum efficiency of 15\% [24] one obtains \( R_0 = 0.75 \text{ nm} \) for glass type S10, which is, within the experimental error, the value derived from dynamic results for high acceptor concentrations [24].

A description of the non-linear decay behaviour was given by Vogler and co-workers [28–31]. They observed comparable phenomena in dye mixtures and colour centre crystals. The more effective transfer at lower acceptor concentrations represented by larger \( k \)-values excludes higher than dipole–dipole transfer mechanisms. More probable is a step-like inhomogeneous spherosymmetric acceptor distribution with a higher acceptor concentration in the vicinity of the donor (Fig. 7). Such a distribution is reasonable because of local disturbance in the bulk material with ion doping leading to a Lenard–Jones-like potential.

The effect is especially remarkable at low acceptor concentrations. As \( r_6 \) approaches infinity (Fig. 7) this gives the dependence of the apparently larger Förster radius \( R_{\text{eff}} \) on the spectrally found one [28–30]:

\[
R_{\text{eff}}^0 = R_0^0 \left( \frac{a}{b} \left[ x_2(t) \right] \right)
\]

with

\[
x_1(t) = \left( \frac{R_0^0}{R_0^0} \right) ^{1/2} \left( t / \tau_D \right)^{1/2}
\]
### TABLE III  Range of enhanced acceptor concentration and factor of enhancement for the energy transfer step \( \text{Cr}^{3+} \rightarrow \text{Yb}^{3+} \)

<table>
<thead>
<tr>
<th>( R_1 ) (nm)</th>
<th>( R_2 ) (nm)</th>
<th>( a/b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.2 to 0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3 to 0.8</td>
<td>1.3 to 1.0</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4 to 0.8</td>
<td>3.0 to 1.1</td>
</tr>
<tr>
<td>0.4</td>
<td>0.5 to 0.8</td>
<td>1.7 to 1.1</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6 to 0.8</td>
<td>2.5 to 1.1</td>
</tr>
</tbody>
</table>

\[
Q[x_i(t)] = 1 - \phi[x_i(t)] + \frac{1 - \exp[-x_i^2(t)]}{\pi^{1/2} x_i(t)} \tag{10}
\]

and

\[
\phi[x_i(t)] = 2\pi^{-1/2} \exp(-u^2) \, du \tag{11}
\]

Now we make the following assumptions.

1. \( t \approx \tau_D \left[ (t/\tau_D)^{1/2} \approx 1 \right] \).
2. Ionic radius of \( \text{Cr}^{3+} < R_1 < R_2 \).
3. \( R_{\text{eff}} = R_0 \) (spectral) \( \approx 0.8 \) nm for \( \text{Yb}^{3+} \) concentrations higher than \( 3 \times 10^{20} \) cm\(^{-3} \).

Assumption 3 means that the enhanced transfer for ions between \( R_1 \) and \( R_2 \) is covered by normal homogeneous-distribution transfer.

From Equation 8,

\[
\frac{a-b}{b} Q_2 - \frac{a}{b} Q_1 = 0 \tag{12}
\]

Equation 12 is satisfied for reasonable values of \( R_1 \) and \( R_2 \) as shown in Table III. From Table III it can be seen that an inhomogeneous distribution of \( \text{Yb}^{3+} \) ions is very probable. The concentration may rise by a factor of 3 in the vicinity of \( \text{Cr}^{3+} \).

### 6. Energy transfer step \( \text{Yb}^{3+} \rightarrow \text{Er}^{3+} \)

The overlap spectra of \( \text{Yb}^{3+} \) absorption and emission together with \( \text{Er}^{3+} \) absorption are given in Fig. 8. Doping of \( \text{Cr}^{3+} : \text{Yb}^{3+} : \) fluoride phosphate glasses with \( \text{Er}^{3+} \) in no case led to a complete abolition of \( \text{Yb}^{3+} \) fluorescence. Best results were obtained for glass type S20 doped with \( 9 \times 10^{20} \) cm\(^{-3} \) \( \text{Yb}^{3+} \) and \( 3 \times 10^{19} \) cm\(^{-3} \) \( \text{Er}^{3+} \). From static fluorescence measurements a transfer efficiency of 73% was derived.

What kind should this second transfer step be? From concentrations of ions one can see that the assumptions of Förster transfer are no longer valid. It must be considered that energy migration within the \( \text{Yb}^{3+} \) system occurs.

Energy migration under the influence of traps is described by the theories of Gochanour, Andersen and Fayer (GAF) [32] and Loring, Andersen and Fayer (LAF) [33]. They used a diagrammatic expansion of the Green function of the donor excitation density \( G^d(r - r', t) \). The advantage of this theory is the \textit{ab initio} calculation of donor excitation. Unfortunately, the results are given as Laplace transforms and must be back-transformed numerically. Federenko and Burshtein (FB) [34] gave an analytical solution for homogeneous and
isotropic media. For low donor excitation the master equations are

$$\frac{d}{dt} p_\text{D}^*(t, R_j) = \sum_{k=1}^{N_D} \left( \frac{\kappa_{\text{DD}}^2}{\tau_D} \right) \left( \frac{R_0^\text{DD}}{r_{jk}} \right)^6 \left[ p_\text{D}^*(t, R_k) - p_\text{D}^*(t, R_j) \right]$$

$$- \sum_{m=1}^{N_A} \left( \frac{\kappa_{\text{DA}}^2}{\tau_D} \right) \left( \frac{R_0^\text{DA}}{r_{jm}} \right)^6 p_\text{A}^*(t, R_j) - \left( 1/\tau_D \right) p_\text{D}^*(t, R_j) \quad j \leq n_D$$

$$\frac{d}{dt} p_\text{A}^*(t, r_m) = \sum_{j=1}^{N_D} \left( \frac{\kappa_{\text{DA}}^2}{\tau_D} \right) \left( \frac{R_0^\text{DA}}{r_{jm}} \right)^6 p_\text{D}^*(t, R_j) - \left( 1/\tau_A \right) p_\text{A}^*(t, r_m) \quad m \leq n_A$$

(13)

with $p_\text{D}^*(t, R_j) = \text{probability of donor excitation at } R_j$, $p_\text{A}^*(t, r_m) = \text{probability of acceptor excitation at } r_m$, $R_0^\text{DD}, R_0^\text{DA} = \text{donor–donor and donor–acceptor Förster radii, respectively}$, $\kappa_{\text{DD}}, \kappa_{\text{DA}} = \text{orientation factors}$ [35].

In the three-body approximation the solutions are [34]

$$D^*(t) = \exp(-qt - t/\tau_D)g(t)$$

(14)

where

$$q = \delta^2/4 - \Gamma(z)$$

(15)

$$g(t) = (a - b)^{-1} \left[ a \exp(a^2 t) \text{erfc}(at^{1/2}) - b \exp(b^2 t) \text{erfc}(bt^{1/2}) \right]$$

(16)
Properties of Cr$^{3+}$ : Yb$^{3+}$ : Er$^{3+}$ : fluoride phosphate glass

and

\[ a = \frac{\sigma_A}{2} + \left( \frac{\sigma_D}{2} \right)[1 - (4/\sigma_D^2)A(z)]^{1/2} \]  
\[ b = \frac{\sigma_D}{2} - \left( \frac{\sigma_D}{2} \right)[1 - (4/\sigma_D^2)A(z)]^{1/2} \]  
\[ \delta = \sigma_D + \sigma_A \]  
\[ \Gamma(z) = A(z) + B(z) \]

A(z) and B(z) are defined as

\[ A(z) = \frac{8}{\pi^2} \left\{ 0.1887 \sigma_D^2 + [0.38320 - \alpha(z)]\sigma_D \sigma_A / 2^{1/2} \right\} \]  
\[ B(z) = \frac{4}{\pi^2} \left\{ 0.3371 \sigma_A^2 - [0.24604 - \beta(z)]\sigma_D \sigma_A / 2^{1/2} \right\} \]

\[ \sigma_D \] and \( \sigma_A \) are dimensionless concentrations as in LAF [33]:

\[ \sigma_D = \frac{(2^{1/3}/3)\pi^2 n_D \kappa_{DD} (R_{0DD}^D)^3 / t_D^{1/2}} \]
\[ \sigma_A = \frac{(2/3)\pi^2 n_A \kappa_{DA} (R_{0DA}^D)^3 / t_D^{1/2}} \]

erfc(z) denotes the complementary error function, and \( \alpha(z) \) and \( \beta(z) \) are tabulated functions of \( z = R_{0D} / R_{DD} \) [33].

According to Equation 7, from Fig. 8 the following transfer radii were derived: \( R_{0DA} = 1.4 \text{ nm} \) and \( R_{0DD} = 1.58 \text{ nm} \) (glass type S15). Orientation factors for homogeneous and isotropic distribution were set to be 0.84 [35].

In Fig. 9 the experimental time behaviour of the Yb$^{3+}$ fluorescence and the results obtained with the help of Equation 14 are shown. The change of decay behaviour with alteration of Yb$^{3+}$ concentration from 0.7 to 1.7 \( \times 10^{21} \text{ cm}^{-3} \) is within experimental error.

![Figure 9](image)

Figure 9 Time dependence of decay of Yb$^{3+}$ fluorescence for different concentrations of Yb$^{3+}$ for glass type S20. \( \tau_D = 1300 \mu s, n_A = 3 \times 10^{18} \text{ cm}^{-3}, n_D = (1) 0.7 \times 10^{21}, (2) 1.3 \times 10^{21}, (3) 1.7 \times 10^{21} \text{ cm}^{-3} \) and (4) Förster case.
In contrast with this, the GAF-LAF-FB theory gives a stronger concentration dependence of the decay, as observed experimentally. Also, a slightly different kinetic is to be seen. However, GAF-LAF-FB theory is in principle a quite valid description of the case handled here.

Differences may be due to the assumption of a homogeneous distribution of donors. Assuming an inhomogeneous distribution of Yb\(^{3+}\) around Er\(^{3+}\) could give a 'saturation' effect and should result in lower sensitivity on changing concentration. However, an analytical back-transformation of solutions of Equation 13 is not possible in this case.

7. Spectroscopic properties of Er\(^{3+}\)

The absorption spectrum of glass type S15 containing \(5 \times 10^{19} \text{ cm}^{-3}\) Er\(^{3+}\) is shown in Fig. 10. The spectrum is corrected for host-glass absorption starting at about 30000 cm\(^{-1}\). The 12 observed absorption bands were used to derive Judd–Ofelt parameters [36, 37]. Transitions with more than 5% overlap were treated as one band. Matrix elements of Carnall et al. [38] were used. The well-known procedure of deriving these parameters can be found elsewhere [39]. It should be noted that some transitions obey relatively strong magnetic dipole character and have to be corrected for this.

The Judd–Ofelt parameter for glass type S15 are as follows:

\[
\begin{align*}
\Omega_2 &= 1.48 \times 10^{-20} \text{ cm}^2 \\
\Omega_4 &= 0.78 \times 10^{-20} \text{ cm}^2 \\
\Omega_6 &= 1.07 \times 10^{-20} \text{ cm}^2
\end{align*}
\]

The r.m.s. error of \(0.3 \times 10^{-20} \text{ cm}^2\) is comparable with ones derived earlier for other host systems [40]. The values for \(\Omega_2\) and \(\Omega_4\) are somewhat lower than that for other glass systems [41, 42].

For the laser transition \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) a radiative lifetime of 8.5 ms was derived. With a measured lifetime of 6.5 ms this yields a quantum efficiency of fluorescence of 76%. The cross-section for stimulated emission, \(\sigma_E\), for this transition could be derived from the

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Properties of Cr\(^{3+}\) : Yb\(^{3+}\) : Er\(^{3+}\) : fluoride phosphate glass

Linewidth $\Delta \nu_{\text{eff}}$ and spontaneous emission probability $A$ according to

$$\sigma_E = \frac{\lambda_p^2}{8\pi n c \Delta \nu_{\text{eff}} A}$$

(25)

With the values of the peak wavelength of $\lambda_0 = 1536\,\text{nm}$, $n = 1.498$, $A = 118\,\text{s}^{-1}$ and $\Delta \nu_{\text{eff}} = 274\,\text{cm}^{-1}$ this yields $\sigma_E = 6.2 \times 10^{-21}\,\text{cm}^2$. This is within experimental error the same value that can be derived from absorption [24].

8. Laser test

For laser test via pumping with a krypton ion laser a conventionally nearly concentric cavity was used. Glass samples of length 4 mm were placed in the centre of this cavity and were pumped longitudinally through the back mirror of the cavity.

The radius of curvature of each mirror was 7.5 cm. The mirrors were highly reflecting for Er\(^{3+}\) laser radiation, and the back mirror was transparent to the pump beam (> 90%). The pump beam was focused with a lens of focal length 7.7 cm. Real c.w. laser action was achieved for glasses containing 10 to 20 mol % phosphates. Best results were obtained with such glasses containing 20 mol % phosphates. For a glass with doping levels of $2 \times 10^{19}\,\text{cm}^{-3}\,\text{Cr}^{3+}$, $9 \times 10^{20}\,\text{cm}^{-3}\,\text{Yb}^{3+}$ and $3 \times 10^{19}\,\text{cm}^{-3}\,\text{Er}^{3+}$ a slope efficiency of 3% with an overall efficiency of 2% was achieved using an output coupling of 2% (Fig. 11).

The lasing wavelength was centred around 1560 nm and was not dependent on the host-glass composition. The bandwidth of the free-running laser was 4 nm. The low efficiency of the system must be ascribed to inhomogeneities of the samples and insufficient cooling.

Because of the broad fluorescence spectrum of Er\(^{3+}\), it was attempted to tune the lasing wavelength. For this purpose a three-mirror folded cavity design with an internal prism as

![Figure 11 Input-output diagram for Er\(^{3+}\) laser action in glass type S20 for different output coupling. For concentrations of ions, see text. $\lambda = 1.56\,\mu\text{m}$.

S119
Figure 12 Tuning range of Er$^{3+}$ for glass type S20. Ion concentrations are $2 \times 10^{19}$ cm$^{-3}$, $9 \times 10^{20}$ cm$^{-3}$ and $3 \times 10^{19}$ cm$^{-3}$ for Cr$^{3+}$, Yb$^{3+}$ and Er$^{3+}$, respectively.

Figure 13 Input-output diagram under flashlamp pumping.
tuning element was used. Within the available pump power the laser was continuously tunable between 1536 and 1596 nm (Fig. 12).

The flashlamp laser test was performed with rods 5 mm × 50 mm and Soviet-type INP 5/60 A–I flashlamps in a conventional pump reflector. With output coupling of 13% (mirror curvature 5 m) and a highly reflecting mirror (curvature 2 m) separated by 40 cm, a slope efficiency of 0.45% and an absolute efficiency of 0.3% could be achieved for a glass type B20 with the reduced Cr<sup>3+</sup> concentration of 1 × 10<sup>19</sup> cm<sup>−3</sup>. The pump pulse duration was 2 ms. For comparison a glass type S20 with double the Cr<sup>3+</sup> concentration is shown.

The higher efficiency with lower Cr<sup>3+</sup> concentration may be due to lower thermal loading. It should be noted at this point that the experimental set-up was optimized neither for output coupling and cooling nor for pump pulse duration. In connection with non-optimized glass production technology, the lower efficiency compared with the phosphate glass rods of Gapontsev et al. [11] becomes understandable and opens the possibility for further increasing of the efficiency.

**8. Conclusion**

Efficient sensitization of fluorescence of Er<sup>3+</sup> in fluoride phosphate glass containing up to 20 mol % phosphates was shown by codoping of Cr<sup>3+</sup> and Er<sup>3+</sup>.

From absorption spectra of Cr<sup>3+</sup> a $Dq/B$-value of 2.04 was derived for these glasses. This low ligand field results in a broad fluorescence of Cr<sup>3+</sup> which overlaps strongly with the Yb<sup>3+</sup> absorption. The energy transfer efficiency between these ions approaches 100%. The deviation of Cr<sup>3+</sup> decay from the well-known Förster law could be understood in terms of inhomogeneous acceptor distribution with an increasing probability for acceptors to be in the vicinity of donors up to a factor of 3. The most efficient transfer is obtained for glasses containing 20 mol % phosphates.

The transfer step Yb<sup>3+</sup> → Er<sup>3+</sup> also shows maximum efficiency for this phosphate concentration. For this transfer step the efficiency is limited to about 75%. The nature of the second transfer step is interpreted in terms of the GAF–LAF–FB theory [32–34] as a migrationally accelerated one.

Judd–Ofelt parameters were derived for Er<sup>3+</sup> in glass type S15. From these parameters a quantum efficiency for Er<sup>3+</sup> fluorescence due to the transition $4^1I_{13/2} \rightarrow 4^1I_{15/2}$ around 1.5 μm of 76% and a cross-section for stimulated emission of $6.2 \times 10^{-21}$ cm<sup>2</sup> was derived.

Real c.w. laser action via krypton laser pumping (647.1 and 676.4 nm) could be achieved, we think for the first time via energy transfer pumping only. In agreement with spectroscopic results, the most efficient system is a fluoride phosphate glass containing 20 mol % phosphates, $2 \times 10^{19}$ cm<sup>−3</sup> Cr<sup>3+</sup>, $9 \times 10^{20}$ cm<sup>−3</sup> Yb<sup>3+</sup> and $3 \times 10^{19}$ cm<sup>−3</sup> Er<sup>3+</sup>. The overall efficiency is limited due to non-optimized glass quality and cooling conditions.

In comparison with Mears et al. [12] the tuning range of the laser output could be doubled. The output was tunable from 1536 to 1596 nm. The limited efficiency of flashlamp pumping should be overcome by optimization of pumping and cooling as well as resonator design.

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