Energy transfer rates of KY$_3$F$_{10}$:Yb:Nd:Tm crystals

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Abstract. In this work we present the spectroscopic properties of KY3F10 (KY3F) single crystals doped with thulium and also co-doped with ytterbium and/or neodymium, KY3F:Yb:Nd:Tm and KY3F:Nd:Tm. The most important processes that lead to the thulium up conversion emissions were identified. The absorption spectra of the samples were measured at room temperature in the range of 200 nm-1200 nm. The emission spectra were obtained by exciting the samples with a 797 nm laser diode and were analyzed using a lock-in amplifier technique. A time-resolved luminescence spectroscopy technique was employed to measure the luminescence decays and to determine the mechanisms involved in the energy transfer up-conversion processes. Analysis of the energy transfer processes dynamics in KY3F:Yb:Tm:Nd crystal, using selective pulsed-laser excitations, shows that the energy transfer from Nd$^{3+}$ to Yb$^{3+}$ ions is the mechanism responsible for the enhancement of the blue up-conversion efficiency when compared with the Yb:Tm system. In the case of KY3F:Nd:Tm it is observed emissions at 350, 355 and 452 nm excited by an additional Yb:Tm step cross relaxation, Yb (2F5/2) → Tm (1G4) that populates the 1D2 (Tm$^{3+}$) excited level. A study of the energy transfer processes in KY3F:Yb:Tm:Nd crystal showed that the 1G4 excited level is mainly populated by the sequence of two nonradiative energy processes that starts well after the Nd$^{3+}$ and Tm$^{3+}$ excitation at 797nm: Nd (4F3/2) → Yb (2F7/2) followed by Yb (2F5/2) → Tm (3H4) → Tm (1G4).

1. Introduction
The study of solids doped with thulium ions has received great interest in the last decades due to the numerous applications of these materials. Concerning to the thulium emission wavelength, these solids can be used as laser materials [10] for different applications in life sciences [11], LIDAR [9] and industry or can be applied as the S-band Tm-doped fiber amplifier (TDFA) in wavelength-division-multiplexing telecommunication [6], or for optical devices [12], color displays [8] and optical memories [7].

Due to the attractive thermo-mechanical properties, wide transparency and high optical damage threshold, KY3F has been studied as laser materials when activated by several RE ions, which can easily substitute for Y$^{3+}$ ions in a non-center-symmetrical site [1] [2-5].
KY3F has relatively low phonon energy (~500 cm\(^{-1}\)) that is an important point in avoiding energy loss by non-radiative relaxation. KY3F is the only compound in the KF–YF\(_3\) system that melts congruently without any phase transition. It crystallizes in the cubic fluorite-type structure (Fm3m) with lattice parameter \(a = 11.54 \text{ Å}\) \([5]\), and the site symmetry of the Yttrium is tetragonal (C\(_{4v}\)) and is isotropic crystals.

In this paper, KY\(_3\)F\(_{10}\) (KY3F) doped with Thulium (Tm) ions that are sensitized by Neodymium (Nd) and Ytterbium (Yb) were studied, and the multiples processes of energy transfer that occurs when these materials are excited around 800 nm were inspected.

2. Experimental Setup
The rare earth fluorides were prepared from pure oxide powders (Alpha-Johnson Matthey, 99.99\%) by hydrofluorination at high temperature in HF atmosphere. The powder was contained in a cylindrical platinum boat, which was inserted in a sealed platinum tube. The LiF-LnF\(_3\) (Ln=Y, Yb, Nd, and Tm) mixture was melted using an open platinum boat in the same atmosphere, with a composition of 1.02 LiF: 1 LnF\(_3\). LiF powder (Alpha-Johnson Matthey, 99.9\%) was zone-refined before it was added to the mixture. The KY3F samples were obtained in the same system by slow cooling. Mixtures of KF-LnF\(_3\) were contained in a cylindrical platinum boat and melted around 990°C and cooled with a rate of \(\sim 10^\circ\text{C/h}\). The synthesized material had always transparent crystalline regions from which the samples were extracted.

The rare earths concentrations were obtained by ICP-OES analysis and yielded the results are shown in the table 1.

| Nominal concentration (mol%) | Measured concentrations (mol%) |
|------------------------------|--------------------------------|
| KY3F:Yb (20.00): Nd (1.30): Tm (0.50) | KY3F:Yb (18.50): Nd (0.91): Tm (0.48) |
| KY3F:Yb (10.00): Nd (1.30): Tm (0.50) | KY3F:Yb (9.25): Nd (0.87): Tm (0.49) |
| KY3F: Nd (1.30): Tm (0.50) | KY3F: Nd (1.25): Tm (0.47) |
| KY3F: Yb (10.00): Tm (0.50) | KY3F: Yb (9.50): Tm (0.48) |

The absorption spectra of all samples were measured in the range 700nm-1000nm at room temperature using a Varian Cary 17D/OLIS Spectrometer. The emission spectra were obtained by exciting the samples that had the same optical thickness, with a SDL diode laser at 797 nm. The emissions of the samples were analyzed with a 0.5 m monochromator (Spex) and a PMT detector. The relative errors in the emission measurements are estimated to be < 5\%. In the lifetime measurements, the samples were excited by pulsed laser radiation generated by a tunable OPO-IR pumped by 2W of Nd:YAG Q-switch laser of 4 ns and 10 Hz. Luminescence signals were analyzed by the 0.25 m Kratos monochromator, detected by the EMI S-20 PMT or InSb 77K infrared detector (Judson) and resolved by the EGG Boxcar Processor. Detector response time was of approximately 0.5 μs. This detector might be pretty slow which could distort the decay curve measurements even in the microsecond time scale and the evaluated decay times might be distorted due to such reason as well.

3. Results and discussion
Optical absorption spectra of KY3F doped Yb:Tm:Nd crystals are shown in Figure 1. This crystal has two main absorptions in the near infrared around 960 nm (Yb\(^{3+}\)) and around 800 nm due to Nd\(^{3+}\) and Tm\(^{3+}\) ions. The most intense absorption is near 960 nm due to high concentration of ytterbium in the samples.
Figure 1. Optical absorption of KY3F crystal doped with neodymium, thulium and ytterbium.

When KY3F crystal containing Tm$^{3+}$ co-doped with Yb$^{3+}$ or Yb$^{3+}$ and Nd$^{3+}$ is excited at 797 nm, ultraviolet (350 nm) and blue (~450 and 480 nm) Tm$^{3+}$ emissions are observed as it can be seen in the Figure 2.

Figure 2. Ultraviolet and blue emission of KY3F:Yb:Tm:Nd, KY3F:Tm:Yb and KY3F:Tm:Nd crystals excited at 797 nm.

As observed in the Figure 2, the Nd (~1 mol%) effect in the KY3F:Yb:Tm:Nd crystal causes an enhancement of the Tm$^{3+}$ blue emission indicating that Nd$^{3+}$ ions significantly contribute to the population of the $^1G_4$ excited level that emits around 480nm. The population of the $^1G_4$ excited level
consequently interacts with $^3\text{F}_{5/2}$ ($\text{Yb}^{3+}$) exciting the $^1\text{D}_2$ ($\text{Tm}^{3+}$) level, which emits near 360 nm and 450 nm.

Figure 3 shows the schematic energy diagram levels of Yb/Tm/Nd system [13] (most of indicated processes will be discussed and proved to be essential for the blue emission up-conversion by the luminescence dynamics analysis in the sequence).

![Figure 3](image_url)

**Figure 3.** Energy levels scheme and energy transfer mechanisms of Yb/Tm/Nd system. Continuous line (up) 797 nm excitation. Dash dot line (down) thulium emissions. Dot lines (up and down) Yb emission and cross relaxation processes.

When the Yb/Tm/Nd sample is excited at 797 nm the following processes are observed to occur:

(a) Ground state absorption of Nd ($^4\text{I}_{9/2}$) → Nd($^4\text{F}_{5/2}$)

(a’) Ground state absorption of Tm ($^3\text{H}_6$) → Tm ($^3\text{H}_4$)

(b) Energy transfer Nd - Yb:

Nd($^4\text{F}_{5/2}$) + Yb ($^2\text{F}_{7/2}$) → Nd($^4\text{I}_{11/2}$) + Yb ($^2\text{F}_{7/2}$)

(c) Back transfer Yb-Nd:

Yb ($^2\text{F}_{7/2}$) + Nd ($^4\text{I}_{9/2}$) → Yb ($^2\text{F}_{7/2}$) + Nd($^4\text{I}_{15/2}$)

(d) Back transfer Tm-Yb:

Tm ($^3\text{H}_6$) + Yb ($^2\text{F}_{7/2}$) → Tm ($^3\text{H}_6$) + Yb($^2\text{F}_{5/2}$)

(e) Cross-relaxation Yb x Tm:

Yb($^2\text{F}_{7/2}$) + Tm ($^3\text{H}_4$) → Yb ($^2\text{F}_{7/2}$) + Tm ($^3\text{H}_4$)

(f) Cross-relaxation Yb x Tm:

Yb ($^2\text{F}_{7/2}$) + Tm ($^3\text{H}_4$) → Yb ($^2\text{F}_{7/2}$) + Tm ($^3\text{H}_4$)

(g) Cross-relaxation Yb x Tm:

Yb($^2\text{F}_{7/2}$) + Tm ($^3\text{H}_4$) → Yb ($^2\text{F}_{7/2}$) + Tm ($^3\text{G}_4$)

(h) Cross-relaxation Yb x Tm:
Yb(\(^{2}F_{5/2}\)) + Tm (\(^{1}G_{4}\)) → Yb (\(^{2}F_{7/2}\)) + Tm (\(^{1}D_{2}\))

(i) Cross-relaxation Nd x Tm:
Nd(\(^{4}F_{3/2}\)) + Tm (\(^{3}H_{4}\)) → Nd (\(^{4}I_{15/2}\)) + Tm (\(^{1}G_{4}\))

(p) Energy transfer Tm-Nd:
Tm (\(^{3}F_{4}\)) + Nd (\(^{1}I_{9/2}\)) → Tm (\(^{3}H_{6}\)) + Nd (\(^{4}I_{15/2}\))

(q) Energy transfer Tm-Nd:
Tm (\(^{3}H_{4}\)) + Nd (\(^{1}I_{9/2}\)) → Tm (\(^{3}H_{6}\)) + Nd (\(^{4}F_{5/2}\))

(r) Cross-relaxation Tm x Tm:
Tm (\(^{3}H_{4}\)) + Tm (\(^{3}H_{6}\)) → Tm (\(^{3}H_{5}\)) + Tm (\(^{3}F_{4}\))

(s) Cross-relaxation Tm x Tm:
Tm (\(^{1}G_{4}\)) + Tm (\(^{3}H_{6}\)) → Tm (\(^{3}H_{5}\)) + Tm (\(^{3}H_{4}\))

3.1. Nd-Yb interaction:
Figure 4 shows the decay time transient of \(^{4}F_{3/2}\) level of Nd\(^{3+}\) measured at 1052 nm and the \(^{2}F_{5/2}\) luminescence decay of Yb\(^{3+}\) (measured at 1000 nm) for Yb(10):Tm(0.5):Nd(1.3):KY\(_{3}\)F\(_{10}\) crystal under 797 nm (a and b) and 960 nm pulsed laser excitations (c).

Best fit of luminescence decay of \(^{4}F_{3/2}\) level (solid line of Figure 4(a)) was done using Inokuti-Hirayama model from where best fitting parameters were \(\gamma = 504 \text{ s}^{-1}\) and \(\tau_{R9} = 334 \text{ ms}\) (integrated decay time was \(\tau_{d9} = 6.5 \text{ ms}\)). Transfer rate of process \(b\) was obtained from the relation \(b = 1/\tau_{d9} - 1/\tau_{R9}\), which gave \(b = 1.15 \times 10^{5} \text{ s}^{-1}\). Figure 4(b) shows that Yb\(^{3+}\) luminescence transient measured at 1000 nm exhibits a raise time of 11 ms consistent with the decay time of Nd\(^{3+}\) excited ions (797 nm). Figure 4(c) shows that the decay time constant of \(^{2}F_{5/2}\) (Yb\(^{3+}\)) level is 753 ms (\(\tau_{d2}\)), which is shorter than the radiative lifetime (1.65 ms). Similarly, the transfer rate of process \(c\) was obtained from the relation \(c = 1/\tau_{d2} - 1/\tau_{R2}\), which gave \(c = 714 \text{ s}^{-1}\).

3.2. Yb-Tm interaction (step 1):
Figure 5 shows the decay time of \(^{3}F_{4}\) luminescence transient of Tm\(^{3+}\) measured at 1900nm.
**Figure 4.** Decay time transient of $4F_{3/2}$ level of Nd$^{3+}$ measured at 1052 nm and the $2F_{5/2}$ luminescence decay of Yb$^{3+}$ (measured at 1000 nm) for Yb(10):Tm(0.5):Nd(1):KY$_3$F$_{10}$ crystal under 797 nm (a and b) and 960 nm pulsed laser excitations (c).
Figure 5. Decay time of $^3F_4$ luminescence transient of Tm$^{3+}$ measured at 1900 nm for Yb(10):Tm(0.5):Nd(1):KY$_3$F$_{10}$ crystal excited by laser pulse at 960 nm.

Best fit of luminescence curve (solid line of Figure 5) was done using two exponentials function $F_i(t) = A \exp(-t/\tau_{\text{rise}}) - \exp(-t/\tau_{\text{decay}})$, where $A$ is a constant, $\tau_{\text{rise}}$ is the luminescence rise time and $\tau_{\text{decay}}$ is the decay time constants. Best fitting parameters found were $\tau_{\text{rise}} = 326$ µs and $\tau_{\text{decay}} = 2.2$ ms. Transfer rate constant of process $e$ was obtained from relation $e = 1/\tau_{\text{rise}} - 1/\tau_{\text{decay}}$. Using $\tau_{\text{rise}} = 753$ µs one gets $e = 1739$ s$^{-1}$. Transfer rate of process $p$ was obtained using the relation $p = 1/\tau_{\text{rise}} - 1/\tau_{\text{radiative}} = 348$ s$^{-1}$, where $\tau_{\text{radiative}} = 9.4$ ms (radiative lifetime of $^3F_4$ level).

3.3. Yb-Tm interaction (step 2):
The $^3H_4$ luminescence decays of Tm$^{3+}$ observed at 800 nm were measured after pulsed laser excitations (960 and 783 nm) and showed in the figure 6.
Figure 6. The $^3H_4$ luminescence decays of Tm$^{3+}$ observed at 800 nm were measured after pulsed laser excitations in Yb(10):Tm(0.5):Nd(1):KY$_3$F$_{10}$ crystal at 960 nm (a) and in Tm(0.5):Yb(10) and Tm(0.5):Nd(1) excited at 783 nm (b).

For this case, the best fit of luminescence curve exhibited in Figure 6(a) was done using the fitting function $F_2(t) = A \left( \exp(-t/\tau_{s5}) - \exp(-t/\tau_{d5}) \right)$, where $\tau_{s5}$ is the luminescence rising time and $\tau_{d5}$ the decay time constants of $^3H_4$ level. Best fitting parameters obtained were $\tau_{s5} = 293 \mu$s and $\tau_{d5} = 476 \mu$s. One may observe that $\tau_{s5}$ is longer than the decay time constant verified for $^3H_4$ level in Tm:Yb:Nd system direct excited at 783 nm giving $\tau_{s5}$ equal to 143 $\mu$s (see Figure 6(b)). However, $\tau_{s5}$ value (293 $\mu$s) is consistent with the expected rise time of a donor like state obtained by multiplication of $^2F_{5/2}$-luminescence decay (Yb$^{3+}$) and the $^3F_4$-luminescence transient (Tm$^{3+}$) (called here $\tau_{s}$ (donor)). Once, we are working with exponentials (see $F_1(t)$), one can deduce that $\tau_{s}$ (donor) is given by

$$
\tau_{s(24)}^{(\text{donor})} = \left[ 1/\tau_{d2} + 1/\tau_{a4} \right]^{-1}
$$

(1)

Using $\tau_{d2} = 753 \mu$s and $\tau_{a4} = 326 \mu$s one gets $\tau_{s(24)}^{(\text{donor})} = 228 \mu$s that is consistent with the experimental value $\tau_{s5} = 293 \mu$s. By the same argument, one can get the decay time constant of the donor like state using that
\[ \tau_{(\text{donor})}^{(24)} = \left( \frac{1}{\tau_{d2}} + \frac{1}{\tau_{d4}} \right)^{-1} \]  

(2)

Using \( \tau_{d2} = 753 \, \mu s \) and \( \tau_{d4} = 2.2 \, \text{ms} \) (both measured in this work) we get \( \tau_{(\text{donor})}^{(24)} = 561 \, \mu s \), which is longer than the experimental value \( \tau_5 = 476 \, \mu s \) obtained from best fitting in Figure 6(a). The transfer rate of process \( f \) can now be calculated using the relation

\[ f = \frac{1}{\tau_5} - \frac{1}{\tau_{(\text{donor})}^{(24)}} = 318 \, \text{s}^{-1} \]  

(3)

Best fit parameters of \( ^3\text{H}_4 \) luminescence decay of Tm:Yb system were \( \gamma = 15.5 \, s^{-1/2} \) and \( \tau_{R5} = 1.14 \, \text{ms} \) given an integrated lifetime \( \tau_{(\text{integrated})}^{(5)} = 830 \, \mu s \). Best fit parameters of \( ^3\text{H}_4 \) luminescence decay of Tm:Nd system were \( \gamma = 96 \, s^{-1/2} \) and \( \tau_{R5} = 1.14 \, \text{ms} \) that gives \( \tau_5 = 143 \, \mu s \) (integrated). The transfer rate of process \( d \) can be calculated using the relation

\[ d = \frac{1}{\tau_{(\text{integrated})}^{(5)}} - \frac{1}{\tau_{R5}} \approx 328 \, \text{s}^{-1} \]  

(4)

where \( \tau_{(\text{integrated})}^{(5)} = 830 \, \mu s \) (Tm:Nd) and \( \tau_{R5} = 1.14 \, \text{ms} \).

Results presented in Figure 6(b) show that the \( ^3\text{H}_4 \) (Tm\(^{3+}\)) excited level is strongly deactivated by Nd\(^{3+}\) ions in Tm:Nd:Yb (process \( q \)) similar to the case of Tm:Nd system. Its rate constant can be calculated from relation

\[ q = \frac{1}{\tau_5} - \frac{1}{\tau_{R5}} \]  

(5)

Using that \( \tau_5 = 143 \, \mu s \) and \( \tau_{R5} = 1.14 \, \text{ms} \) (experimental measures) one gets \( q = 6.12 \times 10^3 \, \text{s}^{-1} \). Tm\(^{(3}\text{H}_4)\):Tm\(^{(3}\text{H}_6)\) cross-relaxation rate (process \( r \)) was calculated using the relation

\[ r = \frac{1}{\tau_5} - \frac{1}{\tau_{R5}} \]  

(6)

Using \( \tau_5 = 830 \, \mu s \) and the radiative lifetime of \( ^3\text{H}_4 \) level (\( \tau_{R5} = 1.14 \, \text{ms} \)) one gets \( r = 328 \, \text{s}^{-1} \).

3.4. Yb-Tm interaction (step 3): The luminescence transient of \( ^1\text{G}_4 \) level of Tm\(^{3+}\) was measured for 797 nm laser pulsed excitation and showed in the Figure 7.
Figure 7. The decay time of $^1\text{G}_4$ luminescence transient of Tm$^{3+}$ excited by pulsed laser at 797 nm was measured for Yb(10):Tm(0.5):Nd(1):KY$_3$F$_{10}$ crystal.

In this case, best fit of luminescence curve (solid line of Figure 7) was done using a fitting function given by

$$F_3(t) = A [\exp(-t/\tau_{66} \cdot \gamma) - \exp(-t/\tau_{d6})],$$  \hspace{1cm} (7)

where $A$ is a constant, $\tau_{66}$ is the rise-time constant of luminescence and $\tau_{d6}$ is the decay-time constant of $^1\text{G}_4$ level (the Burshtein function was used in $F_3(t)$ because the nature of the decay of $^1\text{G}_4$ level that includes a cross relaxation process $s$). Best fitting parameters obtained were $\tau_{66} = 283 \mu$s for the luminescence rising and $\gamma = 6.13 \text{ s}^{-1}$, $w = 538 \text{ s}^{-1}$ and $\tau_{66} = 649 \mu$s for the luminescence decay - integrated decay time constant was $\tau_{d6}^{(\text{integrated})} = 428 \mu$s. It is noticeable that the $^1\text{G}_4$ luminescence generated at expenses of cross interaction between $^1\text{F}_{22}$ (Yb$^{3+}$) and $^3\text{H}_4$ (Tm$^{3+}$) excited levels directly excited by 797 nm pulsed laser excitation can not be produced by Tm$^{3+}$ close by Nd$^{3+}$ ions, because in this case, the decay time of the donor like state obtained is too short, i.e., $\tau_{66}^{(\text{donor})-2} = 1/\tau_{d2} + 1/\tau_{s3}^{-1}$ ~120 $\mu$s compared with the $^1\text{G}_4$ luminescence rise time ($\tau_{66} = 283 \mu$s).

On the other hand, the Tm$^{3+}$ ion close to Yb$^{3+}$ but isolated from Nd$^{3+}$ has a longer lifetime for the $^3\text{H}_4$ level equal to 830 $\mu$s. In this case, the donor like state may have a lifetime of $\tau_{66}^{(\text{donor})-2} \sim 395 \mu$s, which is longer than the rise time constant of $^1\text{G}_4$ luminescence transient (~283 $\mu$s). The transfer rate constant of process $g$ was obtained from relation

$$g = 1/\tau_{d6} - 1/\tau_{66}^{(\text{donor})-2}$$  \hspace{1cm} (8)
where $\tau_{66} = 283$ $\mu$s and $\tau_{66}^{(\text{donor})^2} = 395$ $\mu$s measured for Tm:Yb system, which gave $g = 1000$ $s^{-1}$.

Tm($^4G_4$):Tm($^3H_6$) cross-relaxation rate (process s) was calculated using the decay constant of $^4G_4$ level measured for Tm:Nd:Yb system, where $s = \tau_{66}^{(\text{integrated})} - 1/\tau_{66}$. Using the measured $\tau_{66}^{(\text{integrated})} = 428$ $\mu$s and the radiative lifetime $\tau_{66} = 649$ $\mu$s, we get $s = 796$ $s^{-1}$.

3.5. Yb-Tm interaction (step 4):

The luminescence transient of $^1D_2$ level of Tm$^{3+}$ was measured for 797 nm laser pulsed excitation and showed in the Figure 8.

![Figure 8](image_url)

**Figure 8.** Decay-time transient of $^1D_2$ luminescence from Tm$^{3+}$ measured in Yb(10):Tm(0.5):Nd(1.3):KYF$_{10}$ crystal after 797 nm pulsed laser excitation.

Best fit of luminescence curve (solid line of Figure 8) was done using $F_4(t) = A [\exp(-t/\tau_{\gamma}) - \gamma \sqrt{t} \exp(-t/\tau_{\gamma})]$ where $A$ is a constant, $\tau_{\gamma}$ is the rise-time constant and $\tau_d$ the decay-time of the luminescence transient (the Burshtein function was used in $F_4(t)$ because the nature of the decay of $^4G_4$ level that composes the donor like state $(^2F_{5/2}(\text{Yb}^{3+}) \times ^4G_4(\text{Tm}^{3+}))$). In this case, the radiative lifetime of $^1D_2$ level is too short comparable to the time constant observed in the luminescence transient ($\tau_{\gamma7} = 72$ $\mu$s). Best fit parameters obtained were $\tau_{\gamma} = 224$ $\mu$s (raise-time) and $\tau_d = 302$ $\mu$s, $\gamma = 2.8$ $s^{-1}$, $w = 216$ $s^{-1}$ that gives an integrated decay-time constant equal to $\tau_{d7} = 271$ $\mu$s. These time constants values (measured here) are much closer to the values estimated for the donor like state obtained by the $(^2F_{5/2}(\text{Yb}^{3+}) \times ^4G_4(\text{Tm}^{3+}))$ product that gives $\tau_{d7}^{(\text{donor})} = 205$ $\mu$s (raise-time) and
The lifetime of the excited state of Nd<sup>3+</sup> ions is 6.5 µs. Therefore, process h could not be observed using direct excitation of Nd<sup>3+</sup> and Tm<sup>3+</sup> ions with 797 nm laser excitation because the excited level rapidly transfers its population to the Yb<sup>3+</sup> (~6.5 µs) so triggering process h – process I will be considered negligible in Tm:Nd:Yb:KY3F crystal.

### Table 2. Energy transfer parameters (or rates) of the KY<sub>3</sub>F:Yb:Tm:Nd crystal

| Ions Interaction | Parameter | Rate (s<sup>−1</sup>) | Ions Interaction | Parameter | Rate (s<sup>−1</sup>) |
|------------------|-----------|----------------------|------------------|-----------|----------------------|
| Nd-Yb            | b         | 1.15x10<sup>5</sup>  | Tm-Nd            | p         | 348                  |
| Yb-Nd            | c         | 714                  | Tm-Nd            | q         | 6120                 |
| Tm-Yb            | d         | -                    | Tm-Tm            | r         | 328                  |
| Yb-Tm            | e         | 1739                 | Tm-Tm            | s         | 796                  |
| Yb-Tm            | f         | 318                  | -                |           |                      |
| Yb-Tm            | g         | 1000                 | -                |           |                      |
| Yb-Tm            | h         | -                    | -                |           |                      |

4. Conclusions

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fluoride, chloride, bromide and iodide. Central Glass Co Ltd)
[8] Rao R P 2005 J Lumin 113 271-8
[9] Scholle K, Heumann E and Huber G 2004 Laser Phys Let 1 285-90
[10] Tang Y L, Yang Y, Cheng X J and Xu J Q 2008 Chinese Opt Let 6 44-6
[11] Tollefson M K, Gettman M T and Frank I 2008 J Urology 179 365-
[12] Tsonev L 2008 Opt Mat 30 892-9