Excitation mechanisms of green emission from terbium ions embedded inside the sol-gel films deposited onto nano-porous substrates

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In this work we investigate the excitation mechanism of Tb\textsuperscript{3+} ions in different inorganic sol-gel matrices (composite film of YAlO\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}; Ba\textsubscript{0.6}Sr\textsubscript{0.3}Ca\textsubscript{0.1}:TiO\textsubscript{3}) in porous anodic alumina films. The interest in synthesis of light-emitting materials in porous anodic alumina arises from its unique tailor-made honeycomb structure, strongly enhanced Tb luminescence and great photonic density of states at direction along the channels of the anisotropic light scattering. All discussed sol-gel films were synthesized by spin-on deposition on porous anodic alumina grown on a silicon wafer and annealed at different temperatures. An influence of the annealing temperature on the terbium PL was studied using XRD, 2D photoluminescence excitation and time-resolved spectroscopy. Further, the comparison of thermal quenching data for the most intensive $^5D_4 \rightarrow ^7F_5$ luminescence band and excitation band of Tb \textsuperscript{3+} ions was performed for the temperature range of 10 – 300 K. From the resultant data, mechanisms of Tb excitation and its dependence on the annealing conditions are proposed and discussed.

Introduction

The study of excitation mechanisms of lanthanide ions is a crucial point in the development of the technologies of synthesis in the light-emitting materials, and generation of light using blue and UV incoherent excitation sources. Lanthanide ions can be excited resonantly through $f$-$f$ transitions or $f$-$d$ transitions or non-directly in charge transfer process (CT) or dipole-dipole energy transfer (ET). Nevertheless, in most of matrices into which the lanthanides are introduced only the last three are considered for using as an excitation channel in real devices. The energy position of excitation band related to these process depends strongly on the ions local chemical environment in contrary to well defined excitation bands related to $f$-$f$ transitions. On the other hand, it is already well known that the characteristics of spontaneously emitted light depend strongly on the geometry into which the light source is placed [1, 2]. According to quantum electrodynamics, the emission rate of a two-level quantum emitter, described by Fermi’s golden rule, is generally factorized into a part describing the sources’ intrinsic quantum properties (in our case described by Judd-Ofelt theory) and another part describing the influence of the environment on the light field. Currently, there are many efforts to control the emission rate of quantum emitters by optimizing the nanoscale
environment by, e.g., reflecting interfaces [3], microcavities [4], photonic crystals [5, 6], or plasmonic nanoantennae [7]. Thus, combination of interesting properties of lanthanides with possibilities given by for example photonic crystals to control these properties seems to very interesting from the point of view of fundamental physics as well potential applications.

Thus, in this work we present an optical investigations of optical properties of Tb$^{3+}$ ions doped into different matrices embedded inside the nano-porous matrix and we will investigate the influence of the matrix on their excitation mechanism.

**Experimental details**

In the experiments, superpure aluminium was magnetron-sputtered onto a planar side of a polished wafer of monocrystalline silicon. Aluminium was completely anodized in a 1.2 M orthophosphoric acid solution at a constant temperature of 17°C and constant voltage 130 V. From scanning electron microscopy, the PAA thickness was 9 μm and the average pore diameter was 140 nm. Yttrium-alumina oxides were prepared using stage-by-stage dissolution of nitrate salts (Sigma Aldrich) Y(NO$_3$)$_3$ × 4H$_2$O (99.99% purity), Al(NO$_3$)$_3$ × 9H$_2$O (98 % purity) and Tb(NO$_3$)$_3$ × 5H$_2$O (99.9 purity) in an aqueous-alcoholic solution, with pH adjusted to 2 with diluted nitric acid. As a stabilizer, citric acid in the molar ratio [metal ions]/[citric acid] = 1/3 was used.

The starting materials were barium acetate [Ba(CH$_3$COO)$_2$], strontium acetate hemihydrate [Sr(CH$_3$COO)$_2$·1/2H$_2$O], calcium acetate monohydrate [Ca(CH$_3$COO)$_2$·H$_2$O], terbium acetate hydrate [Tb(CH$_3$COO)$_3$·3,3H$_2$O] and titanium isoproxide {Ti(OCH(CH$_3$)$_2$)}$_4$. Glacial acetic acid (CH$_3$COOH) and 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH) were used as solvents. The Ba acetate, Sr acetate, Ca acetate and Tb acetate were dissolved in acetic acid and refluxed at 110 °C for 0,5 h. After cooling down to room temperature, Ti isoproxide, dissolved in 2-methoxyethanol, was added to the solution. The mixed solution was refluxed and then acetylacetone (CH$_3$COCH$_2$COCH$_3$) and water were added to the solution for stabilization and hydrolysis, respectively.

Terbium-containing solution was deposited on porous anodic alumina by sequential spinning at a rate of 2700 rpm followed by drying at 200 °C and a final 30-min annealing at temperatures up to 1100°C. The average size of the sample was about 1 x 1 cm$^2$. Incident light from the xenon lamp (450W) from the monochromator (Jobin Yvon TRIAX 180) was focused on the sample. The photoluminescence and the photoluminescence excitation signals were collected and transmitted by an optical fiber to the spectrometer (HR4000 Ocean Optics) and divided by the light source characteristic. The flash xenon lamp and strobe detector coupled with monochromators were used to observe the time-resolved spectra.
Obtained results

Figure 1 shows PL spectra of Tb-doped BST, YAG films annealed at 900°C and Tb ions introduced directly into PAA matrix and annealed at 800°C obtained for the excitation wavelength of 270 nm. For all samples, four main PL bands, associated with the f-f internal orbital transitions of Tb$^{3+}$ ions are clearly resolved. They can be related to the radiative transitions from the $^5D_4$ state to $^7F_J$ ($J = 6, 5, 4, 3, 2$) states of Tb$^{3+}$ at 493, 543, 584, 620, 700 nm, respectively. Moreover, for Tb$^{3+}$ ions doped into YAG sample emission also reveal weak blue emission bands, related to transitions from the $^5D_3$ state to $^7F_J$ ($J = 6, 5, 4$) states of Tb$^{3+}$ at 384, 416, 438 nm, respectively. Nevertheless, for all fabricated samples, the $^5D_4 \rightarrow ^7F_5$ (543 nm) electric dipole transition is the most intensive. Moreover, what can be seen from Fig. 1 is that only for Tb$^{3+}$ ions introduced into the YAG matrix the emission lines are characterized by a well resolved Stark lines while for other samples the emission line is characteristic for the ions in glass matrix or other words ions are placed in many different sites. Additionally, what is not seen from the Fig. 1 the emission intensity for Tb ions in BST and YAG sample is almost the same while the signal coming from Tb$^{3+}$ ions directly deposited onto PAA substrate is weaker by one order of magnitude.
In order to analyze the excitation mechanisms of Tb ions embedded in different matrices and to compare the influence of the matrix on these mechanisms, the total photoluminescence excitation spectroscopy (TPLE) has been used. Figure 2 (a) shows the 2D-PLE map of Tb$^{3+}$:BST/PAA film structure annealed at 900°C. The colors of the map correspond to the PL intensity plotted as a function of both excitation and emission wavelengths. The main three optical transitions, e.g. $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$ discussed above, are well resolved. Similar maps were obtained for all fabricated samples, and the TPLE data were obtained by calculating the integral over the emission wavelengths for the observed emission bands fitted by the Gaussian curves for each excitation wavelength.

For Tb$^{3+}$ ions deposited directly onto PAA substrate the most efficient excitation band appear at 230 nm through the allowed $f$-$d$ transition from $^5F_1$ level to $5d_2$ [LS] state within the Tb$^{3+}$ ion, while the excitation band at 270 nm related to allowed $f$-$d$ transition from$^3F_1$ level to $5d_1$ [LS] characterize by a very weak intensity. Nevertheless, when the Tb$^{3+}$ ions are introduced into the YAG matrix, and then deposited onto PAA substrate, the situation became opposite and the main excitation band is due to allowed $f$-$d$ transition from $^5F_1$ level to $5d_1$ [LS] state. Moreover, in this case an additional excitation band appears at ~320 nm which band can be related to $f$-$d$ forbidden high-spin transition from $^5F_1$ level $5d_1$ [HS] state. This differences are due to strong modifications of the local crystal field surrounded Tb$^{3+}$ ions (its strength and symmetry) what strongly influences the selection rules for optical transitions within the Tb$^{3+}$ ion. Additionally, as it has been discussed in details by Dorenbos [8] position of the first $f$-$d$ transitions (for Ce$^{3+}$)
depending on the matrix composition. This effect can be also seen in our case, when the maximum of the excitation bands is blueshifted by 10 nm (175 meV) when Tb$^{3+}$ ions are introduced into the YAG matrix. Nevertheless, one should be pointed out here, that in the case of Tb$^{3+}$ ions directly deposited onto PAA substrate we don’t have a model situation reflected a free Tb$^{3+}$ ion states. This is because the oxidation process for the lanthanides is very efficient and most probably Tb$_{x}$O$_{y}$ phase is formed at the PAA surface.

Moreover, the broadening of all excitation bands for both samples differ and band related to transition from $^5F_1$ level to 5d$_1$ [LS] state became almost three times narrower when introduced Tb$^{3+}$ ion inside the matrix while the higher transition seems to not change to much for both samples. This is mostly because the electron-phonon coupling is different for both samples what should be also observed in modifications in radiative decay rates. Detailed analyzes of excitation mechanism of Tb$^{3+}$ in YAG matrix and its dependence on the annealing temperature can be found elsewhere [9].

When comparing discussed up to now excitation spectra with ones obtained for Tb$^{3+}$ introduced into the BST matrix, we can conclude that most probably all three 5d transitions observed for YAG matrix participate in the excitation of Tb$^{3+}$ ions but their broadening is significant and at room temperature there is no possibility to resolve them and to discus each excitation band separately. Nevertheless, it seems that the main contribution is coming also like in the case of Tb ions in YAG matrix from allowed low-spin transition from $^5F_1$ energy level to 5d$_1$ [LS] state of Tb$^{3+}$ ion. It is worth to notice here that the excitation spectrum for Tb$^{3+}$ ions in BST matrix is a bit more difficult task since strong defect related emission appears at the excitation wavelengths longer then 330 nm, which emission overlap spectrally with one from Tb ions and can be seen from Fig.2 (a). More details about this issue and TPLE calculations for Tb$^{3+}$ in BST matrix can be found elsewhere [10].

To analyze the influence of the matrix on the excitation mechanism of Tb ions in more details, all excitation spectra have been fitted by Gaussian curves and obtained parameters have been listed in Tab.1.

<table>
<thead>
<tr>
<th>TABLE I. Fitting parameters obtained from TPLE measurements.</th>
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<tr>
<td>Matrix</td>
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<tr>
<td>-----------------</td>
</tr>
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</tr>
<tr>
<td>YAG</td>
</tr>
<tr>
<td>BST</td>
</tr>
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</table>

In the last step, we have investigated the influence of the matrix composition on the kinetic properties of Tb$^{3+}$ ions. For this purpose, all samples have been excited at 270 nm and obtained in this way decay curves for the most intense $^5D_4$ - $^7F_5$ transition have been shown in Fig. 3 (a). In order to fit all data, as a starting point the Maximum Entropy Method (MEM) has been used [11]. This model assumes that the emission arising from different Tb$^{3+}$ sites is characterized by a distribution of decay rates (discrete distribution spaced logarithmically), which is expected here due to variation in local crystal filed surrounding ions. The advantage of this method is that no luminescence decay model or physical model of the material (assuming recombination rates distribution) is required a priori. The resultant distributions of decay times are given in Fig. 3 (b). Nevertheless, to get more physical intuition from obtained by us data, in the next step, it has been
proposed to fit the obtained data by a stretch exponential function (called also Kohlrausch-Williams-Watts (KWW) function) defined as follow

\[ I_{PL}(t) = (\alpha A) \cdot (At)^{\alpha-1} \exp\left(-\left(At\right)^{\alpha}\right) \]  

[1]

where parameter \( A = 1/\tau_{PL} \) and \( \alpha \in (0, 1) \) describes the distribution of decay rates [12] and \( \langle \tau_{PL} \rangle = \frac{\tau_{PL}}{\alpha} \left(\frac{1}{\alpha}\right) \) gives the information about the averaged decay time characterized investigated system. To get a perfect agreement between the experimental data and fitting curves and taking into account the results obtained from MEM model where two main decay times distributions have been obtained for each sample, the double stretch function (d-KWW) has been used for fitting obtained decay data. Calculated from the fitting parameters averaged decay times \( \langle \tau_{PL} \rangle \) have been marked in the Fig 3.(b) as bars on top axis and listed in Tab. 2.

\[ \text{Figure 3. (a) PL decay times measured at 270 nm excitation wavelength for Tb}^{3+} \text{ ion in YAG, BST matrix and directly deposited onto PAA substrate together with a d-KWW fitting curves, (b) decay times distributions obtained by using MEM model together with averaged decay times obtained from d-KWW analysis marked as bars.} \]

Obtained from MEM model results are somehow surprising since the shortest decay time (~1000 µs) has been obtained for Tb\(^{3+}\) ions deposited directly onto PAA substrate for which, at assumption that there is no matrix around the ion, the decay time should tend to infinity since this transition for a free ion (in full spherical symmetry site) is formally forbidden. When introducing Tb\(^{3+}\) ions inside the BST and YAG matrix the decay time increases by factor ~2 and ~4, respectively. This result can be explained when we will analyze the kinetic of Tb\(^{3+}\) ions not from the point of view of local symmetry but
rather from the point of view of local vibronic environment. As it has been mentioned previously, most probably Tb$^{3+}$ ions at the PAA surface are strongly coupled to many OH molecules which are well known from the fact that they strongly quench the emission from the lanthanides and modifies their kinetic due to overlapping of their oscillating modes with the energies between the levels of lanthanide ions. This conclusion is in good agreement with the TPLE spectra when the excitation band at 270 nm is almost three times narrower for Tb$^{3+}$ placed in YAG matrix as compared with deposited onto PAA substrate only, what means that the electron-phonon coupling is much smaller in this case and consequently the recombination time should be longer as it has been observed from our results. This conclusion can be also confirmed by observation of higher in energy transitions within the ion ($^7D_3 \rightarrow ^7F_1$) for YAG matrix and most probably also for BST matrix where they are overlapped giving one broad and weak emission band. Appearance of these emission bands means that the relaxation of excited carriers is not completed to the lowest $^5D_4$ level what can suggest that the coupling between excited electrons and phonons is not so efficient as in the case of Tb deposited onto PAA substrate only. From Fig.3(b) it can be also seen that the distribution of decay times for Tb$^{3+}$ ions in different matrices also vary from sample to sample and the best homogeneity has been found for Tb$^{3+}$ ion YAG matrix. To analyze these results more quantitatively all decay curves have been fitted by Eq.1 and obtained parameters have been collected in Tab.2.

It can be seen that $\alpha$ parameter for YAG sample is $\sim$0.9 what is higher then $\alpha \sim 0.8$ and 0.7 parameter for BST and PAA sample reflecting results obtained from MEM model where decay time distribution narrowing also with the same trend as $\alpha$ increasing. Moreover, values of $\alpha$ for all samples are close to 1, what indicates that the distribution of Tb$^{3+}$ sites, reflected as the main contribution to observed emission is quite narrow and can be characterized by the Gaussian distribution. Also averaged decay times $<\tau_{PL}>$ follow the same trend as ones obtained from MEM model. However, when analyzing the second decay time contribution to the total emission decay signal it can be seen that it is characterize by a wide distribution of decay times (very small $\alpha$ parameter) indicating variety of Tb$^{3+}$ sites. In this case, comparison between the parameters obtained from MEM model and the data taken from KWW function are not in very good agreement. This is most probably due to the fact that the distribution of Tb$^{3+}$ sites in this case must be described by more complicated distribution for which fitting by a KWW function does not apply.

<table>
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<tr>
<th>Matrix</th>
<th>Decay times KWW-1</th>
<th>Decay times KWW-2</th>
<th>Decay times MEM</th>
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<td></td>
<td>$\tau_1(\mu s)$</td>
<td>$\alpha_1$</td>
<td>$\tau_2(\mu s)$</td>
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<td>1103</td>
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<tr>
<td>BST</td>
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</tr>
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<td>YAG</td>
<td>989</td>
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<td>3693</td>
</tr>
</tbody>
</table>

Acknowledgments

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References

8. P. Dorenbos, Phys.Rev.B 64 125117 (2001), and references there in.