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Energy transfer processes in $Sr_3Y(PO_4)_3$ eulytite singly doped and co-doped with Tb^{3+} and Tm^{3+}

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In this work the optical spectroscopy and the energy transfer processes involving the Tb^{3+} and Tm^{3+} ions, have been studied in eulytite double phosphate hosts of the type $Sr_3Y(PO_4)_3$ doped with various amounts of the two lanthanide ions. It has been found that several energy transfer and cross-relaxation processes are active in this class of materials, upon excitation in the $^5D_4$ level of Tb^{3+}, and in the $^1G_4$ one of Tm^{3+}. In particular, a $Tb^{3+} \rightarrow Tm^{3+}$ transfer of excitation has been found to quench strongly the $^5D_4$ level of Tb^{3+}. This process occurs with a transfer efficiency increasing from 0.08 to 0.62, for a donor concentration of 2 mol%, and an acceptor concentration increasing from 2 to 15 mol%. The emission spectra are strongly affected by the presence of $Tb^{3+} \rightarrow Tm^{3+}$ energy transfer, and $Tm^{3+} \rightarrow Tm^{3+}$ cross relaxation processes.

Keywords: energy transfer, lanthanide ions, luminescence, phosphate materials, optical spectroscopy.

Introduction

The non-radiative transfer of excitation involving trivalent lanthanide ions has been intensively studied since the early 1960s [1–3] but still attracts a lot of attention due to unanswered questions regarding the mechanisms at play [4], and the technological applications of this type of processes [5,6]. The energy transfer Tb.Tm has been documented and investigated in the past, but special emphasis was given to the use of these ions in crystalline or non-crystalline materials in order to produce white light (when co-doped with other suitable ion(s)) [7–9], or enhanced emission in the near IR region [10]. Apart from these studies pointing at interesting applications of these phenomena, not many investigations have dealt in a detailed way with the basic mechanisms dealing with the transfer mechanisms involving Tb^{3+} and Tm^{3+} [9,11–23]. In recent times, our group has studied energy transfer processes involving Tb and another lanthanide ion in eulytite-type cubic materials with formula $A_3M(PO_4)_3$ (A = divalent cation, M = trivalent cation) [24–27]. We found interesting to extend these investigations to (Tb, Tm) co-doped eulytites in order to contribute to the understanding of the $Tb^{3+} \rightarrow Tm^{3+}$ transfer processes, and evidence the impact of the crystal structure on the transfer efficiency and mechanism. In this contribution we shall focus on the energy transfer from the donor $^5D_4$ level of Tb^{3+} to the acceptor Tm^{3+} ion. Additional results will be presented in a future paper [28].

Experimental

A series of singly doped and co-doped eulytites $Sr_3Y_{1-xy}Tb_xTm_y(PO_4)_3$, ($x = 0$, 0.01, 0.02; $y = 0$, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.15) was synthesised in polycrystalline form by solid state reaction at high temperature (1250°C, 48 h) as previously described [23]. X-ray diffraction patterns, luminescence spectra and decay curves were measured as described in ref. [27].

Results and discussion

All samples under investigation were found by powder X-ray diffraction (PXRD). to be single phase with a cubic eulytite phases (space group $I\bar{4}3d$) [29]. No impurity phases were observed.

The energy level diagram of the Tb^{3+} and Tm^{3+} ions is shown in Fig. 1. The emission and excitation spectra of the singly doped eulytites are presented in Fig. 2 and 3. Following excitation at 486 nm (20580 cm^{-1}) in the 5D4 level, the sample $Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ shows the usual emission transitions $^5D_4 \rightarrow ^7F_J$ ($J = 0$–5) in the region 520–700 nm (Fig. 2), whilst upon 463 nm excitation (21598 cm^{-1}, in the $^1G_4$ level) $Sr_3Y_{0.99}Tm_{0.01}(PO_4)_3$ gives rise to two bands assigned to the transitions $^1G_4 \rightarrow ^3F_4$, and $^1G_4 \rightarrow ^3H_5$, located at 650 and 787 nm (15380 and 12710 cm^{-1}) respectively (Fig. 3) The latter assignment [30] is proposed assuming that cross-relaxation has a minor impact and multiphonon relaxation from $^1G_4$ is negligible, due to the low concentration of Tm, and to the fact that the Raman spectrum of the phosphate eulytites has typically a high energy peak in the range from 950 to 990 cm^{-1} [31], implying that more than six vibrational quanta are required to bridge the $^1G_4$–$^3F_2$ energy gap of Tm^{3+}, amounting to almost 6200 cm^{-1} [32].

The decay curve of the $^5D_4$ level of Tb^{3+} in $Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ was measured at RT upon excitation

at 486 nm and emission at 543 nm. It is perfectly exponential with an observed decay time of 2.79 ms (Fig. 4).

Conversely, the RT decay profile of $^1G_4$ of Tm^{3+} in $Sr_3Y_{0.99}Tm_{0.01}(PO_4)_3$, measured upon excitation at 464 nm and with emission at 650 nm (Fig. 5) is distinctly non-exponential, presumably due to several almost resonant cross-relaxation mechanisms such as:

$$^1G_4(Tm) + {}^3H_6(Tm) \rightarrow {}^3F_2(Tm) + {}^3F_4(Tm), \quad (1)$$
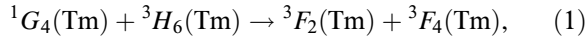
already operative at low Tm concentrations [31,33]. A precise analysis of this decay curve is beyond the scope of this paper; the first e-folding time of this decay is 0.33 ms. For the sake of comparison, the radiative lifetime of $^1G_4$ in cubic Y_2O_3 is 0.408 ms [34].

The RT emission spectrum in the region 515−850 nm o f a representative Tb/Tm co-doped sample is shown in Fig. 6 upon excitation at 486 nm into $^5D_4$ (Tb).

The spectrum is composed of emission bands assigned to the $^5D_4 \rightarrow {}^7F_J$ transitions of Tb^{3+} discussed above, without clear evidence of bands ascribable to Tm^{3+}. On the other hand, the $Tb^{3+} \rightarrow Tm^{3+}$ energy transfer was previously found to occur based on the resonant mechanism [12]:

$$^5D_4(Tb) + {}^3H_6(Tm) \rightarrow {}^7F_0(Tb) + {}^3F_3(Tm). \quad (2)$$
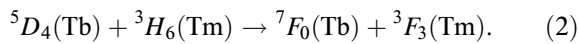
This mechanism populates the $^3F_3$ level of Tm^{3+}, which then relaxes rapidly in a non-radiative way to the $^3H_4$ level, which in principle should give rise to emission around 790 nm, due to the $^3H_4 \rightarrow {}^3H_6$ transition. This transition is not clearly visible in the present emission spectra, presumably because an additional energy transfer ($Tm^{3+} \rightarrow Tb^{3+}$) process takes place, which depopulates the $^3H_4$ level [13]:

$$^7F_6(Tb) + {}^3H_4(Tm) \rightarrow {}^7F_0(Tb) + {}^3F_4(Tm). \quad (3)$$
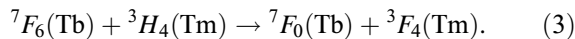
The eventual detection of emission from $^3F_4$ (around $1.75 \mu m$) is prevented by spectral limitations of our equipment.

The decay curves of the $^5D_4$ emission of Tb^{3+}, obtained upon excitation at 486 nm, are shown in Fig. 7, for all samples containing 2 mol% of Tb, and 0, 2, 3, 5, 7 10 and 15 mol% of Tm.

A complete analysis of these curves is beyond the scope of this paper, but it is clear that co-doping with Tm^{3+} quenches the Tb^{3+}, and therefore the mechanism (2) described above is operative. The e-folding times of the 5D4 decays are reported in Table 1. A more detailed analysis of these decay curves will be reported elsewhere.

The energy transfer efficiencies η_T can be approximately estimated using [34]:

$$\eta_T = 1 - \tau_{Tb-Tm}/\tau_{Tb}, \quad (4)$$

where τ_{Tb-Tm} is the e-folding time of the $^5D_4$ decay in the presence of Tm^{3+} Values for various samples are also reported in Table 1.
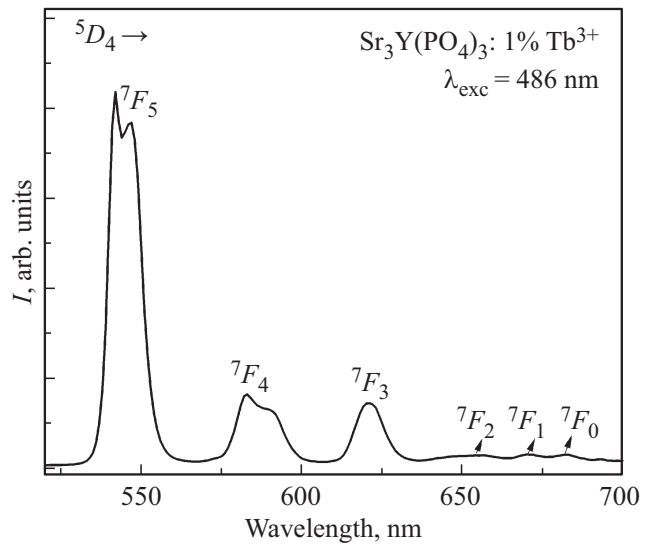

Figure 2. Luminescence spectra of $Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ at room temperature at excitation at a wavelength of 486 nm.

Inspection of the Table shows that in the presence of a relatively low Tb^{3+} donor concentration the energy transfer efficiency seems to increase significantly with the increasing concentration of the Tm^{3+} acceptor. This is indicative of the fact that the assistance of energy migration is not necessary to realize relatively fast $Tb^{3+}-Tm^{3+}$ energy transfer, in agreement with previous studies [12]. More detailed studies about the energy transfer processes responsible for the quenching of the $^5D_4(Tb^{3+})$ emission are under way and will be presented elsewhere [28].
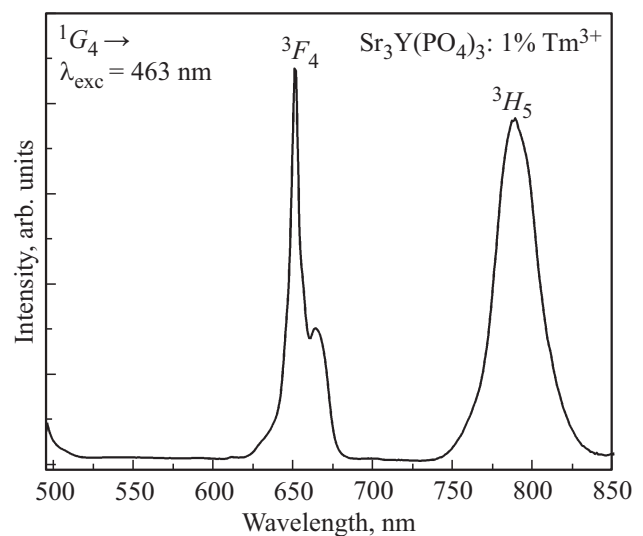

Figure 3. Luminescence spectra of $Sr_3Y_{0.99}Tm_{0.01}(PO_4)_3$ at room temperature at excitation at wavelength of 463 nm.
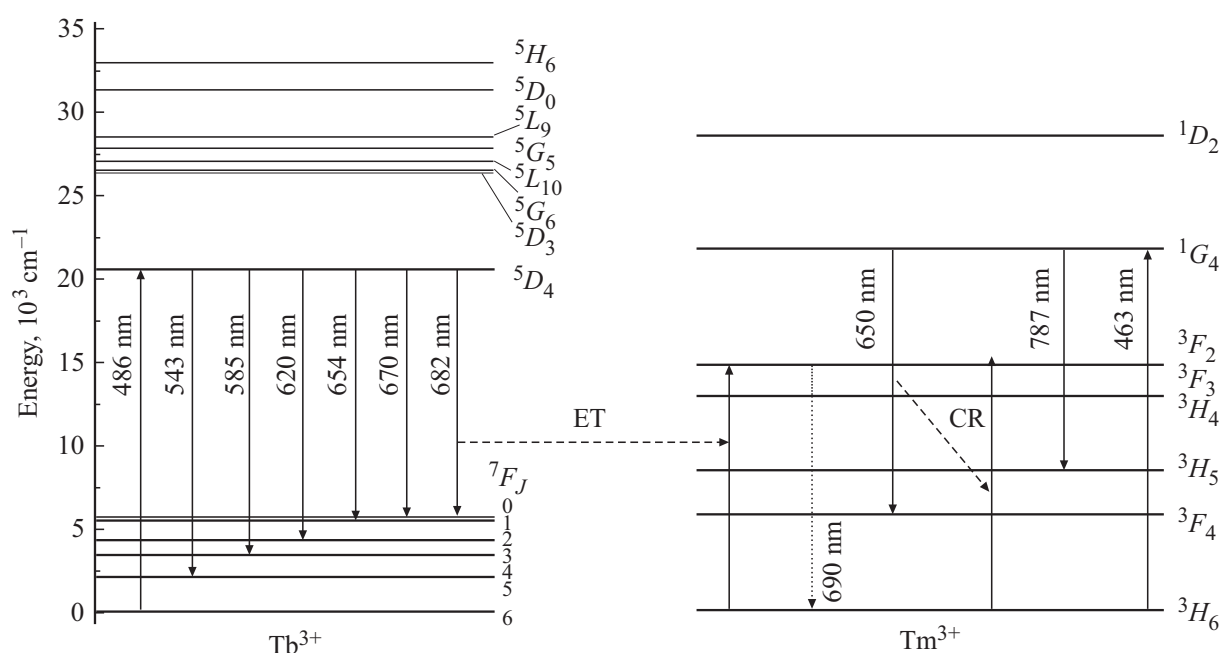
Figure 1. Scheme of energy levels, energy transfer and cross-relaxation pathways for Tb^{3+} and Tm^{3+} ions discussed in the text.
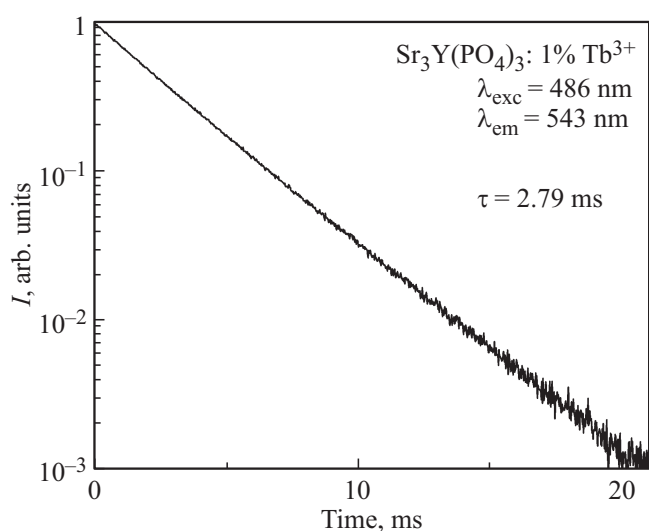

Figure 4. Luminescence decay curve of $Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ at room temperature. Exciting light wavelength is 486 nm, registered luminescence — 543 nm.

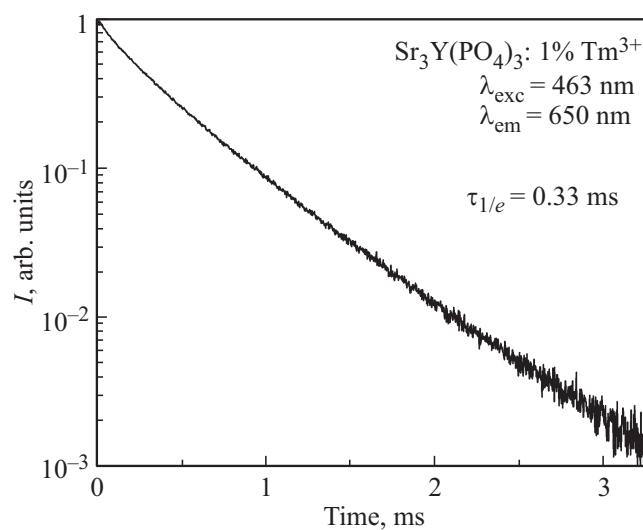**Figure 5.** Luminescence decay curve of $Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ at room temperature. Exciting light wavelength is 463 nm, registered luminescence — 650 nm.

Conclusion

Energy transfer processes involving the Tb^{3+} and Tm^{3+} ions have been studied at room temperature in eulytite double phosphate materials with stoichiometry $Sr_3Y_{1-x-y}Tb_xTm_y(PO_4)_3$, ($x = 0$, 0.01, 0.02; $y = 0$, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.15). The spectroscopic results and the excited state dynamics have shown that, in the present experimental conditions, the Tb3+.Tm3+ energy transfer and internal Tm3+.Tm3+ cross relaxation processes take place upon excitation in the emissive

5D4(Tb3+) level belonging to the 4f8 configuration. The quenching of the 5D4(Tb3+) emission by the Tm3+ acceptor appears to be rather efficient for a donor (Tb3+) concentration of 2 moladditional channels of excitation transfer occurring upon excitation in other energy levels, such as 1G4 of the Tm3+ ion. The investigation of these additional processes lies beyond the scope of the present paper and will be presented elsewhere [28]. It is anyway already possible to conclude that the Tb/Tm system is characterized by a multitude of relaxation pathways, possibly more complex than for other pairs of lanthanide ions.

Initial luminescence decay time ($\tau_{1/e}$) from the level $^5D_4$ and efficiency η_T of energy transfer $Tb^{3+} \rightarrow Tm^{3+}$ described by equation (3), in samples $Sr_3Y_{0.98-y}Tb_{0.02}Tm_y(PO_4)_3$

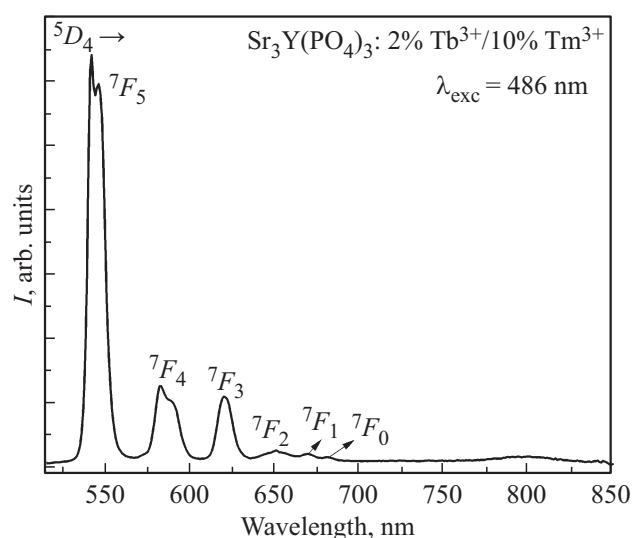| y	$\tau_{1/e}(^5D_4)$, ms	η_T
0	2.78	–
0.02	2.55	0.08
0.03	2.39	0.14
0.05	2.11	0.24
0.07	1.88	0.32
0.10	1.53	0.45
0.15	1.05	0.62

Figure 6. Luminescence spectra of $Sr_3Y_{0.88}Tb_{0.02}Tm_{0.10}(PO_4)_3$ at room temperature during excitation at wavelength of 486 nm.
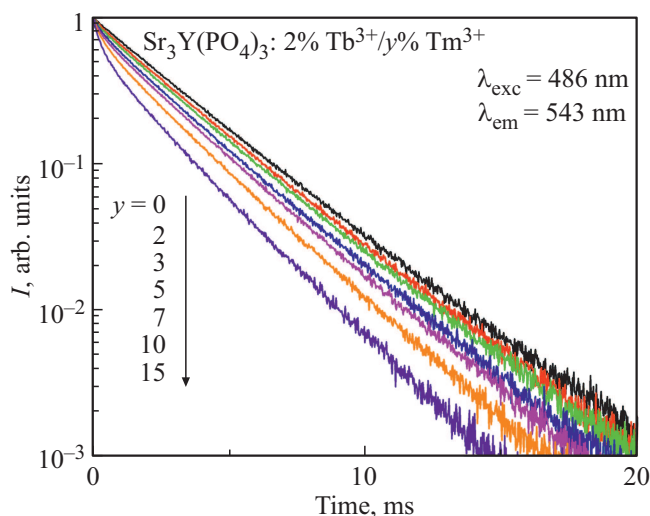

Figure 7. Radiation decay curves from the level $^5D_4$ of the Tb^{3+} ion, obtained upon excitation at wavelength of 486 nm, for all samples containing 2 mol% Tb and 0, 2, 3, 5, 7, 10 and 15 mol.% Tm.

The processes of energy transfer involving Tb^{3+} and Tm^{3+} ions in eulytite double phosphates with stoichiometry of $Sr_3Y_{1-x-y}Tb_xTm_y(PO_4)_3$, ($x = 0$, 0.01, 0.02; $y = 0$, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.15) were studied at room temperature. The study results of the spectra and dynamics of the excited state showed that under the given experimental conditions, upon excitation to the radiative level $^5D_4(Tb^{3+})$, related to the configuration $4f^8$, the processes of energy transfer $Tb^{3+} \leftrightarrow Tm^{3+}$ and internal cross-relaxation ($Tm^{3+} \rightarrow Tm^{3+}$) occurred. The radiation quenching from the level $^5D_4(Tb^{3+})$ by the Tm^{3+} acceptor turns out to be sufficiently effective at the donor concentration (Tb^{3+}) 2 mol%. Preliminary results gave the presence of a number of additional channels for excitation transmission, which arise upon excitation to other energy levels such as level $^1G_4$ of the Tm^{3+} ion. The study of these additional processes is beyond the scope of this paper and will be presented in another paper [28]. In any case, we can conclude that the Tb/Tm system is characterized by many relaxation paths, possibly more complex than for other pairs of lanthanide ions.

Acknowledgments

Funding

Conflict of interest

The authors declare that they have no conflict of interest.

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