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A spectroscopic study of K_2YF_5:Pr^{3+}

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Abstract

$(Pr^{3+})^1D_2$-red emission and $(Pr^{3+})^3P_0$-blue emission are observed in K_2YF_5:Pr^{3+} under $^3P_{0,1}$ and $^1D_2$ excitations. Based on the analysis of the relative emission intensities and the luminescence decays we have concluded that both phenomenon occur respectively by means of cross-relaxation, rather from $^3P_1$, and up-conversion energy transfer. Such effects have been linked to Pr^{3+} ion-clustering favoured by the 1D-character of the structure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The trivalent praseodymium-doped solids are known to be attractive energy up-conversion media leading to potentially simultaneous blue, green and red emissions offering applications such as solid state lasers for display and optical data storage [1,2]. Such interest is characterised by the importance of the subject of research focussed in the two directions: (i) development of efficient emitting materials, notably by analysing the role of the host materials and (ii) investigation of the de-excitation channels of the excited states and the resulting Stokes and anti-Stokes energy transfer routes.

Due to their low phonon energy resulting in low multiphonon relaxation rates and high emission efficiencies, the fluoride compounds appear suitable to contribute to analyse the aforementioned points.

Among the fluorides, compounds of the composition K_2LnF_5 (Ln=rare earth) are the least studied, due to the difficulty of their preparation system.

The K_2LnF_5 phases crystallise in the orthorhombic (Ln=Y) and hexagonal (Ln=Pr) systems, respectively. Each Y^{3+} ion is surrounded by seven fluoride ions in a C_{2v} local point symmetry. The YF_7 polyhedra form chains parallel to the *c*-axis of the structure. Doping of the compound by Pr^{3+} ions occurs without deformation of the structure up to 5 mol.% Pr^{3+}.

In this paper we report the measurements of luminescence spectra and time characteristics after selective excitations in the $^3P_1$, $^3P_0$ and $^1D_2$ levels. The dependence of the luminescence profiles, emission and decays, with the excitation wavelengths, have been discussed in the framework of Pr^{3+} ions clustering in relation with the 1D-character of the structure.

2. Experimental

Powder samples were prepared by solid state reaction as described in [3]. The obtained compounds were checked by X-ray powder diffraction and IR absorption spectroscopy. The Pr^{3+} concentration was determined by chemical analysis. The luminescence spectra and decay curves were recorded using a set-up described in [4].

3. Results and discussion

Laser-induced emission spectra of K_2YF_5:Pr^{3+} consist of a large number of narrow bands, the intensity of which depends upon the concentration of Pr^{3+}, the temperature and the excitation wavelength. Analysis of these spectra, as well as the excitation spectra related to the transitions $^3H_4 \rightarrow {}^1D_2$, $^3P_{0.1}$, $^1I_6$ [5] performed at 15 K have allowed to determine the energies of the Stark components of the main electronic states of Pr^{3+} in this compound. The

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Table 1
Stark components of some energy levels of trivalent praseodymium in K_2YF_5 at 15 K

Level	$^1I_6$	$^3P_1$	$^3P_0$	$^1D_2$	$^3H_6$	$^3H_4$
Energy (cm^{-1})	21583, 21598, 21634, 21647, 21659, 21721	21385, 21407, 21437	20912	16634, 16857, 17146, 17439	4240, 4261, 4369, 4438, 4498, 4568, 4581, 4589, 4615, 4623, 4629, 4657	0, 16, 172, 323, 508, 595, 644, 730, 767,
Barycenter (cm^{-1})	21640	21410	20912	17019	4506	417

results obtained for some levels for K_2YF_5:0.1 mol.% Pr^{3+} are reported in Table 1.

3.1. Blue excitation

Emission spectra in the red wavelength range, of K_2YF_5:0.1 mol.% Pr^{3+} excited at 21 385 cm^{-1} (467.6 nm — $^3P_1$) and 20 912 cm^{-1} (478.2 nm — $^3P_0$) are depicted in Fig. 1. Direct population of $^3P_0$-state at low temperature does not give rise to emission from $^1D_2$-state while this is clearly observed via $^3P_1$-state. By increasing the temperature, above 100 K typically, both $^3P_0$ and $^3P_1$ excitation lead to the observation of emission from $^1D_2$-state (Fig. 1c). A similar but less pronounced increase in the intensity of $^1D_2$-emission is observed at 15 K by increasing the Pr^{3+} concentration above 0.5 mol.%. Observation of rise times on the $^1D_2 \rightarrow {}^3H_4$ luminescence decays as shown on the insert of Fig. 1, much longer under $^3P_0$ excitation (a) than $^3P_1$ (b), excitation reinforce the conclusion that population of $^1D_2$-state takes place via $^3P_1$ rather than $^3P_0$-state.

The above observations suggest phonon-assisted cross-relaxation mechanism giving rise to emission form $^1D_2$-state after blue excitation. Such cross-relaxation can be accounted as follows:

$$Pr^{3+}(^3P_1) + Pr^{3+}(^3H_4) \rightarrow Pr^{3+}(^1D_2) + Pr^{3+}(^3H_6) + \Delta E_1 \qquad (1)$$

$$Pr^{3+}\,(^3P_1) \rightarrow Pr^{3+}\,(^3P_0) + \Delta E_{1\text{-}0} \qquad (2)$$

The value of ΔE_1 is about 317 cm^{-1} and can be taken up easily since the phonon cut-off estimated in K_2YF_5:Eu^{3+} is of about 450 cm^{-1} [6]. Process (2) is a very efficient multiphonon relaxation process. Process (1) competes effectively at relatively high concentration of

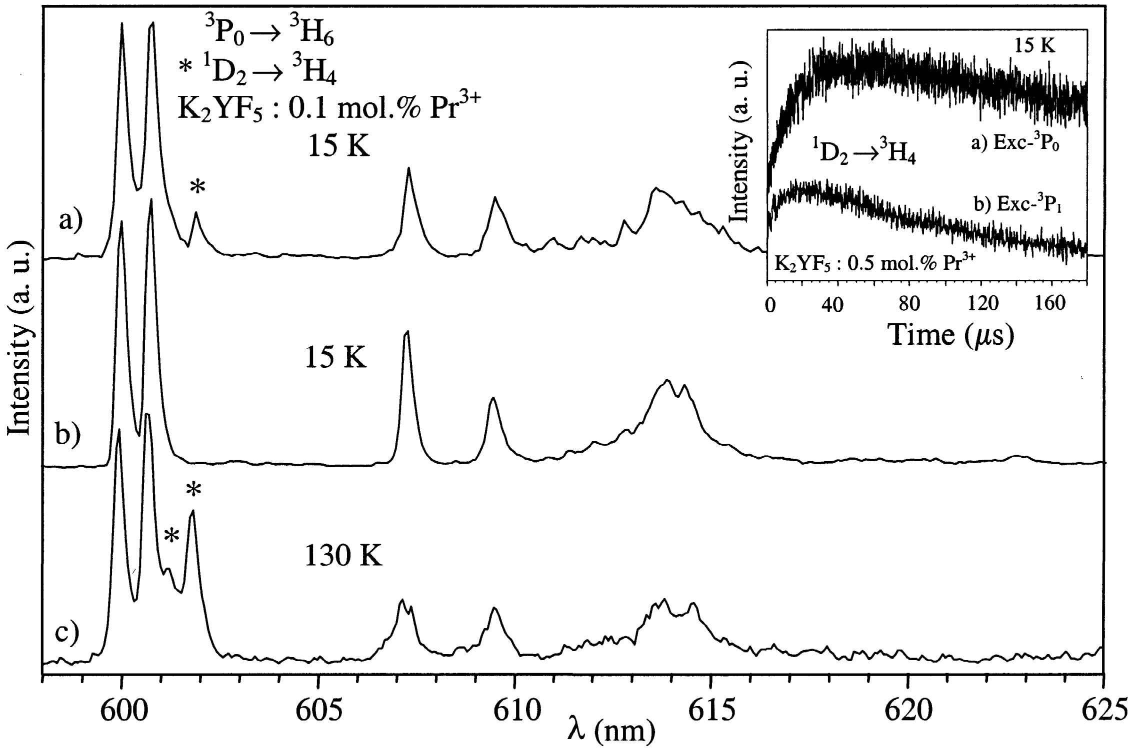

Fig. 1. $^3P_0 \rightarrow {}^3H_6$ and (*) $^1D_2 \rightarrow {}^3H_4$ emission spectra of K_2YF_5: 0.1 mol.% Pr^{3+} under selective excitation into the $^3P_1$ state (a) at 15 K and into the $^3P_0$ state (b) at 15 K, (c) at 130 K. The insert represents the $^1D_2 \rightarrow {}^3H_4$ luminescence decays of K_2YF_5:0.5 mol.% Pr^{3+} at 15 K under (a) $^3P_0$ and (b) $^3P_1$ selective excitation.

Pr^{3+}. Nevertheless ion clustering is a favourable case which can notably enhance the efficiency of process (1) even in weakly doped materials. This is what is observed in CaF_2:Pr^{3+} for example [7]. In K_2YF_5, effect of ion clustering is probably produced by the 1D character of the structure inducing a non-random distribution of the Pr^{3+} centres along the *c*-axis. However by increasing the temperature, an equilibrium is established between the populations of $^3P_1$ and $^3P_0$ states enhancing the efficiency of process (1) which can in that case explain observation of $^1D_2$-emission following excitation in the $^3P_0$.

3.2. Orange–yellow excitation

Under laser excitation tuned to the $^1D_2$ level, up-converted emission from the $^3P_0$ state was generated between 15 K and 300 K. A quadratic dependence of the overall blue $^3P_0 \rightarrow {}^3H_4$ emission on the laser input power was determined. This indicates that two-photon processes are involved in this system.

The up-converted emission spectra have the same line shape and peak position as under blue excitation when the excitation is produced in the centre of the main $^3H_4 \rightarrow {}^1D_2$ absorption bands. However the $^3H_4 \rightarrow {}^1D_2$ excitation spectra show satellite bands. Because they are very weak, even in the more concentrated samples, a quantitative analysis of the variation of their intensity relative to that of the main peaks with concentration is difficult. However it seems that their intensity grows with increasing Pr^{3+} concentration. Excitation in these satellites produce up-converted emission spectra which differ slightly from the formers notably in the peak position, but with increased number of transitions leading to total degeneracy of the electronic transitions.

Evolution of the luminescence decays of the blue and orange–yellow emissions under $^3P_0$ and $^1D_2$ excitations with the concentration of Pr^{3+} ions and the temperature will be the subject of subsequent paper. However direct excitations in the $^3P_0$ and $^1D_2$ levels produce nearly exponential Stokes decays at 15 K for the more diluted sample (0.1 mol.%) with time constants of 35 μs and 580 μs for $^3P_0$ and $^1D_2$, respectively. Fig. 2 reports the time evolution of the blue emission arising from the $^3P_0$ state under $^1D_2$ excitation at 15 K for K_2YF_5:0.1 mol.% Pr^{3+} (the figures at the right side represent the decays recorded at short time scale).

Depending on the excitation wavelength the decay shapes differ notably. When the excitation is produced at the centre of the $^1D_2$ absorption band the $^3P_0$ emission shows clearly a rise time (~13 μs) which becomes very short (~0.8 μs) if the excitation coincides with the satellites denoted A and C on Fig. 2. At long times we find the value of 30 μs and 93 μs, respectively, for the A and B excited luminescence decays.

Such situation was observed firstly in LaF_3:Pr^{3+} [8] and has been explained arguing the existence, in the material, of class of ions, especially pairs, between which energy transfer is very active. This assumption seems operative in our case since the 1D-structure, as we have suggested before, is propitious for existence of distributions of neighbouring ions along the chains in a random way.

Based on the lifetime measurements, a direct two-photon absorption process is unlikely, since for this mechanism the up-converted decay of the $^3P_0 \rightarrow {}^3H_4$ emission would be identical to the lifetime of the directly excited $^3P_0$ level. Therefore, using the Energy Transfer Up-conversion (ETU) model developed for Pr^{3+} in several compounds as schematically represented in the right hand of Fig. 3, the shapes of luminescence decays were tentatively discussed. The discrepancies noted in the literature concerns especially the label of the intermediate state (I) related to the first step process since generally the $^1G_4$ or $^3H_6$ states are considered [8].

In the framework of the ETU process, independently of the intermediate state, the respective populations N_2 and N_0 of the $^1D_2$ and $^3P_0$ states follow the equations:

$$\dot{N}_2 = -W_2 N_2 - 2W_t N_2^2 \qquad (3a)$$

$$\dot{N}_0 = -W_0 N_0 + W_t N_2^2 \qquad (3b)$$

Where W_0, W_2 are the decay rates of levels $^1D_2$ and $^3P_0$ and W_t the transfer rate [8].

Eq. (3b) has been numerically integrated to fit the experimental decays of the $^3P_0 \rightarrow {}^3H_4$ emission under $^1D_2$ excitation. Fig. 3 reproduces the fit obtained for K_2YF_5:0.1 mol.% at 15 K under excitation at centre of the $^3H_4 \rightarrow {}^1D_2$ excitation band using the experimental values $W_0^{-1} = 35$ μs and $W_2^{-1} = 580$ μs mentioned before with W_t as fit parameter. The result is quite satisfactory particularly for the rise time. The derived transfer rate was $W_t = 1.5 \times 10^4$ s^{-1}. For the decays recorded by exciting in the satellite bands a disagreement between the experimental curves and the theoretical fits was noted using the former set of W_0^{-1} and W_2^{-1} values. However good fit is obtained both for A and C excited luminescence decays using $W_0^{-1} = 17$ μs and $W_2^{-1} = 290$ μs, corresponding to the half of the previous values (Fig. 4), and in that case the transfer rate was $W_t = 5 \times 10^7$ s^{-1}.

Although the latest-mentioned values are subject to discussion, they have the advantage to support hypothesis of existence of clusters in which efficient energy transfer occurs leading to fast population of the $^3P_0$ state which decays with time constant close to that obtained by direct excitation.

In conclusion, $^3P_1$-cross-relaxation mechanism and $^1D_2$-up-conversion energy transfer leading to direct feeding of $^1D_2$-state and $^3P_0$-state, respectively, have been accounted to explain the low-temperature emission properties of K_2YF_5:Pr^{3+} under blue and orange laser excitations. The 1D character of the structure of the material has been

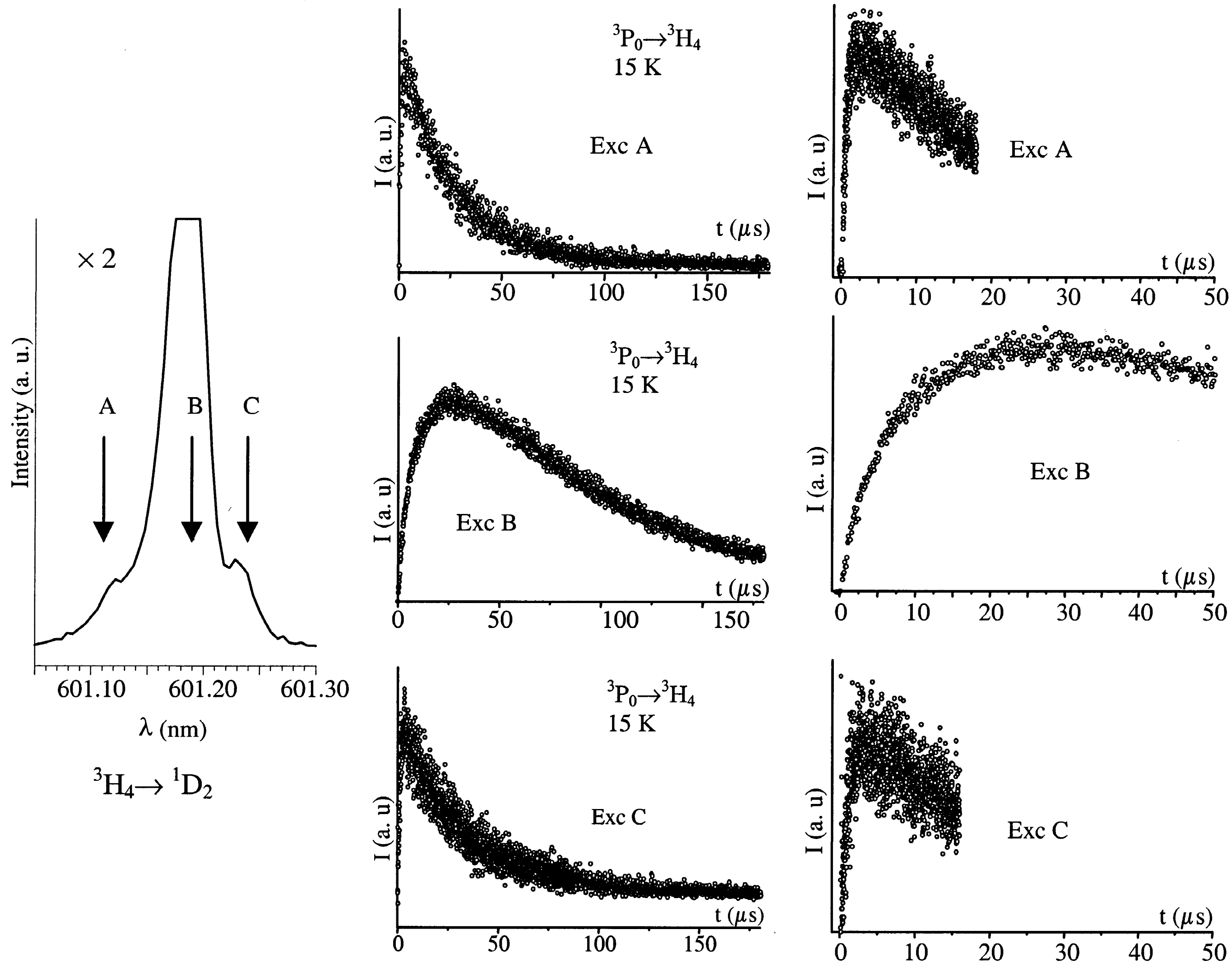

Fig. 2. Up-converted decay profiles of the $^3P_0 \rightarrow ^3H_4$ emission of K_2YF_5:0.1 mol.% Pr^{3+} at 15 K under several excitations into the $^3H_4 \rightarrow ^1D_2$ absorption, (A) Exc = 601.11 nm, (B) Exc = 601.19 nm and (C) Exc = 601.24 nm.

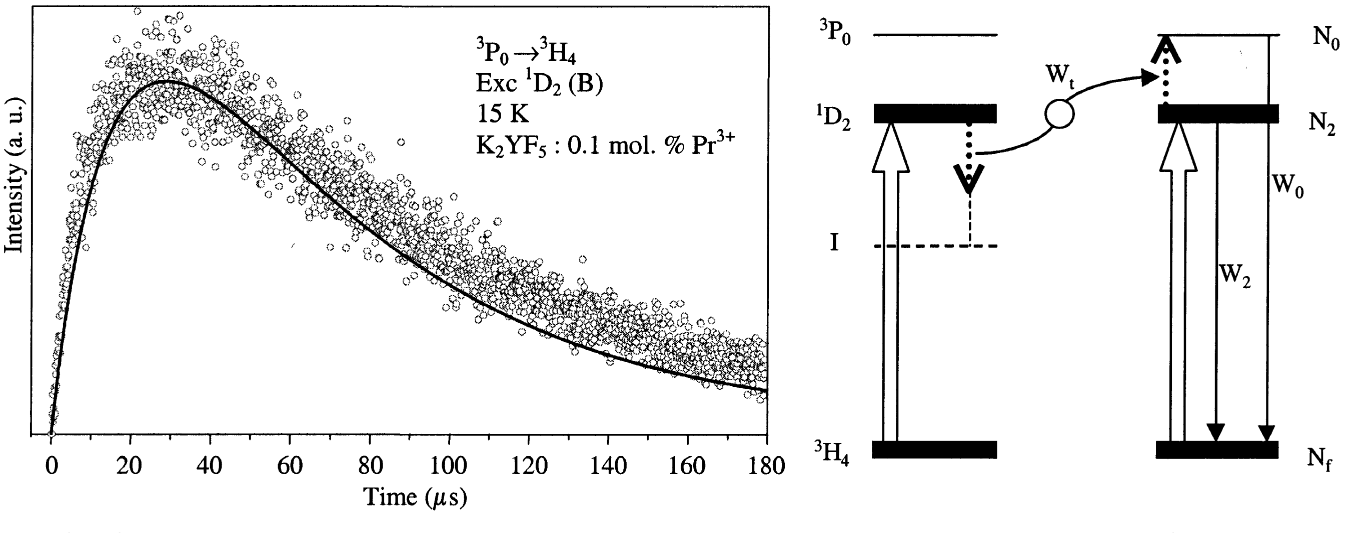

Fig. 3. $^3P_0 \rightarrow ^3H_4$ up-converted ($^1D_2$ — B) (oooo) experimental and (—) calculated decays using Eq. (3b) for K_2YF_5:0.1 mol.% Pr^{3+} according to the up-conversion energy transfer model depicted on the right hand of the figure. Parameters of the fit are discussed in the text.

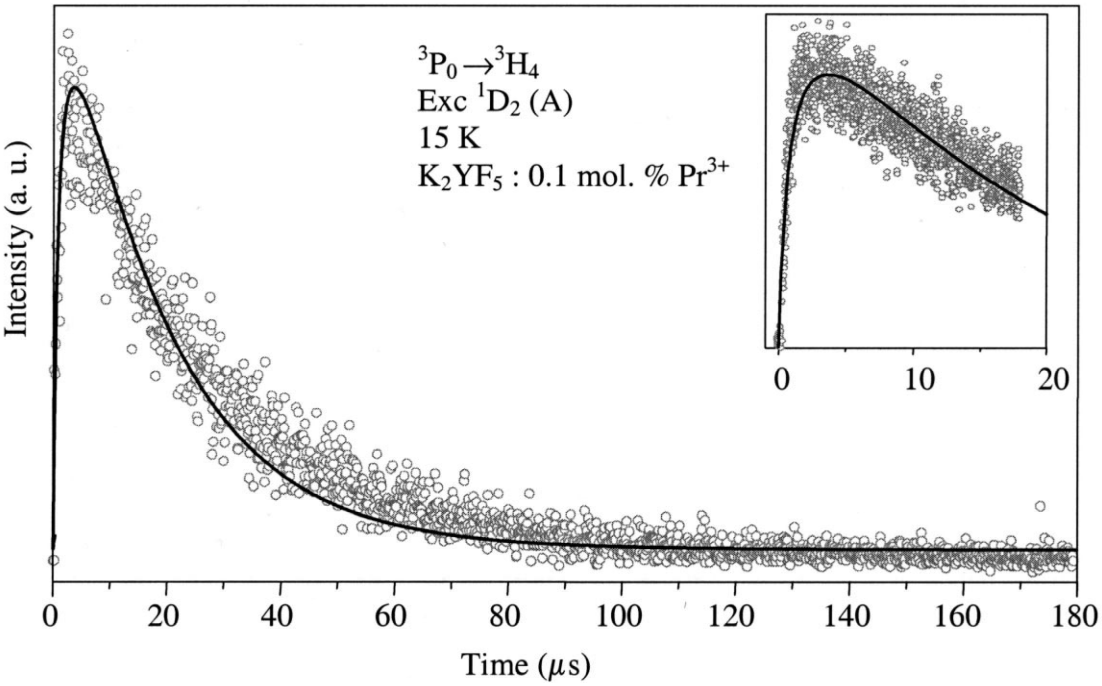

Fig. 4. $^3P_0 \rightarrow {}^3H_4$ up-converted ($^1D_2$ — A) (oooo) experimental and (—) calculated decays using Eq. (3b) K_2YF_5:0.1 mol.% Pr^{3+}. Parameters of the fit are discussed in the text.

considered as an important parameter to explain the efficiencies of both phenomena.

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