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Non-radiative fast processes and quantum efficiency of transition metal ions in solids

M. Grinberg^{a,*}, A. Mandelis^b^a*Institute of Physics, N. Copernicus University, Grudziadzka 5/7, 87-100 Torun, Poland*^b*Photothermal and Optoelectronic Diagnostics Laboratory, Department of Mechanical Engineering, University of Toronto, Toronto M5S 1A4, Canada*

Abstract

In this contribution we investigate the dependence of quantum efficiency of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ on the wavelength of the exciting light. We consider fast non-radiative transitions between the highly excited vibronic states of the system and slow non-radiative and radiative processes which take place in the system thermalized in the first excited state. The results of our model calculations are compared with photopyroelectric spectra of $\text{Ti}^{3+}:\text{sapphire}$.

1. Introduction and the model description

The aim of this paper is to analyze the non-radiative processes and quantum efficiency of the Ti^{3+} ion in sapphire. However the model elaborated in this paper can be easily extended to other systems characterized by strong electron–lattice coupling. The Ti^{3+} ion in Al_2O_3 is a d^1 system, with the electronic structure consisting of ${}^2\text{E}$ excited and ${}^2\text{T}_2$ ground state, with large Jahn–Teller $E^*\varepsilon$ effect in the excited state [1]. The significant offset between the energy minima of the ground and excited electronic manifolds results in large probability of non-radiative internal conversion process [1].

To calculate the efficiency of the radiative and non-radiative processes, we assumed that emission of photons occurs only when the excited system is thermalized, whereas the non-radiative transitions can take place from an arbitrary excited vibronic

state of the ${}^2\text{E}$ electronic manifold. One distinguishes fast processes, which occur “before” the excited system reaches the thermal equilibrium and slow processes which take place “after” this fact. There are two fast non-radiative processes; the intra-configurational process during which the system relaxes, step by step, from the $|{}^2\text{E}, n\rangle$ to the $|{}^2\text{E}, n-1\rangle$ state, by means of emission of a phonon, and the inter-configurational non-radiative internal conversion process in which the electronic configuration of the system is changed from e to t_2 , without changing the energy ($|{}^2\text{E}, n\rangle$ to $|{}^2\text{T}_2, m\rangle$ radiationless transitions). If the inter-configurational non-radiative internal conversion occurs, further relaxation of the system to the ground state, $|{}^2\text{T}_2, 0\rangle$ (also a fast process), is only radiationless. Intra-configurational non-radiative transitions cause the non-radiative relaxation of the system to the metastable state, $|{}^2\text{E}, 0\rangle$. In this case, further relaxation occurs by radiative and non-radiative transitions. We consider the latter processes to be slow because they are characterized by time

* Corresponding author.

constants many orders of magnitude larger than fast non-radiative processes. The above-mentioned radiationless fast processes have been considered by Seelert and Strauss [2] as responsible for non-radiative transitions between excited states of Cr^{3+} system in fluorescence materials. In this paper we give a detailed description of their kinetics.

2. Kinetics of de-excitation and quantum efficiency calculation

Assuming that the incident light (constant or long duration pulse excitation) of intensity $I_{\text{ex}}(\hbar\Omega)$ converts the system to the $|^2\text{E}, n\rangle$ state, the kinetics of the de-excitation is given by the following set of coupled equations:

$$I_{\text{ex}}(\hbar\Omega)\beta(\hbar\Omega) = (N_n - M_m)P(E \rightarrow T)_{\text{inter}}^{nm} + N_n P(E)_{\text{intra}}^n, \quad (1a)$$

$$0 = (M_m - N_n)P(T \rightarrow E)_{\text{inter}}^{mn} + M_m P(T)_{\text{intra}}^m, \quad (1b)$$

$$N_n P(E)_{\text{intra}}^n = (N_{n-1} - M_{m-1})P(E \rightarrow T)_{\text{inter}}^{n-1, m-1} + N_{n-1} P(E)_{\text{intra}}^{n-1}, \quad (1c)$$

$$M_m P(T)_{\text{intra}}^m = (M_{m-1} - N_{n-1})P(T \rightarrow E)_{\text{inter}}^{m-1, n-1} + P(T)_{\text{intra}}^{m-1}, \quad (1d)$$

$$\vdots \quad \quad \quad \vdots \quad \quad \quad \vdots$$

$$N_{t+1}P(E)_{\text{intra}}^{t+1} = N_t P_{\text{nr}}^t - M_k P(E \rightarrow T)_{\text{inter}}^{kt} + N_t P_{\text{rad}}^t, \quad (1e)$$

$$M_{k+1}P(T)_{\text{intra}}^{k+1} = M_k P(T \rightarrow E)_{\text{inter}}^{kt} - N_t P_{\text{nr}}^t + M_k P(T)_{\text{intra}}^k. \quad (1f)$$

Here $\beta(\hbar\Omega)$ is the absorption coefficient, N_n and M_m are the occupation numbers of the n th vibronic state related to the excited electronic manifold, ^2E , and of the m th vibronic state related to the ground electronic manifold, $^2\text{T}_2$, respectively. $P(E \rightarrow T)_{\text{inter}}^{nm}$ and $P(T \rightarrow E)_{\text{inter}}^{mn}$ are the probabilities of the internal conversion transitions between the excited and ground, and ground and excited electronic manifolds, respectively, $P(E \rightarrow T)_{\text{inter}}^{nm} = P(T \rightarrow E)_{\text{inter}}^{mn}$. $P(T)_{\text{intra}}^m$ and $P(E)_{\text{intra}}^n$ are the probabilities of intra-configurational non-radiative transitions “inside”

the ground and excited electronic manifolds, respectively. Both, inter- and intra-non-radiative processes mentioned above are fast. N_t is the occupation number of the thermalized excited system, P_{rad}^t and P_{nr}^t are the radiative and non-radiative transition probabilities, which describe the de-excitation of the thermalized system. These processes are slow.

One can calculate the quantum efficiency of the system, η_{R} , by dividing the number of emitted photons, $N_{\text{phot}} = N_t P_{\text{rad}}^t$, by $I_{\text{ex}}(\hbar\Omega)\beta(\hbar\Omega)$. Because usually $P(E \rightarrow T)_{\text{inter}}^{ij} \ll P(E)_{\text{intra}}^i$ one can assume that $N_i \gg M_j$ for any i and j . This allows us to decouple Eqs. (1) and we obtain:

$$\eta_{\text{R}}^{\text{Ti}}(\hbar\Omega, T) = \left[\prod_{k=1}^{n(\hbar\Omega)} \frac{P(E)_{\text{intra}}^k}{P(E \rightarrow T)_{\text{inter}}^{kl} + P(E)_{\text{intra}}^k} \right] \times \frac{P_{\text{rad}}^t}{P_{\text{rad}}^t + P_{\text{nr}}^t(T)}. \quad (2)$$

Since η_{R} depends on the probabilities of fast processes, $P(E)_{\text{intra}}^k$ and $P(E \rightarrow T)_{\text{inter}}^{kl}$, through a product of n components, where n increases with $\hbar\Omega$, a significant decrease of $\eta_{\text{R}}^{\text{Ti}}$ is expected for excitation to large n even if $P(E \rightarrow T)_{\text{inter}}^{kl}$ is small in comparison with $P(E)_{\text{intra}}^k$. Since $\Omega = 2\pi c\lambda^{-1}$, where c is the speed of light and λ is the wavelength, one can express the quantum yield as a function of λ .

To obtain the $\eta_{\text{R}}^{\text{Ti}}(\lambda, T)$, we calculated the non-radiative transition probability $P_{\text{nr}}^t(T)$, and the internal conversion probabilities $P(E \rightarrow T)_{\text{inter}}^{ij}$ using the Struck and Fonger [3] approach extended to a two-dimensional harmonic oscillator.

$$P_{\text{nr}}^t(T) = \tau_0^{-1} \sum_n \sum_{k'=0}^m \sum_{k=0}^n \times \delta(E_e^n - E_g^m) |F_{\text{eg}}^{n-k, m-k'}|^2 |F_{\text{eg}}^{kk'}|_{\perp}^2 S^n(T) \quad (3)$$

and

$$P(E \rightarrow T)_{\text{inter}}^{nm} = \tau_0^{-1} \sum_{k'=0}^m \sum_{k=0}^n \times \delta(E_e^n - E_g^m) |F_{\text{eg}}^{n-k, m-k'}|^2 |F_{\text{eg}}^{kk'}|_{\perp}^2, \quad (4)$$

where e and g denote the excited ^2E and the ground $^2\text{T}_2$ electronic manifold, respectively. In the case of Ti^{3+} ion the non-radiative transitions between the

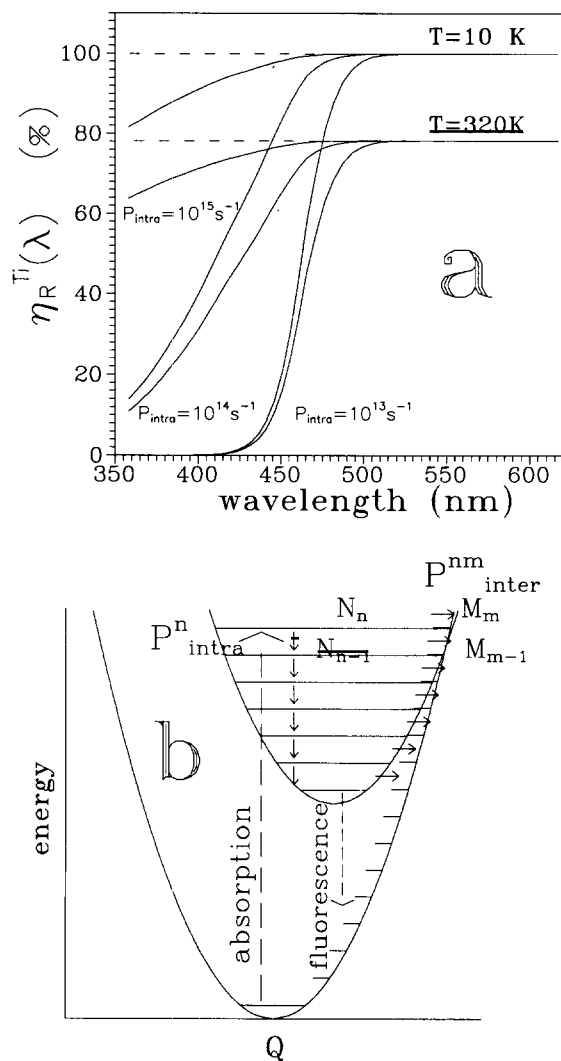


Fig. 1. (a) The radiative quantum efficiency of Ti^{3+} in Al_2O_3 versus excitation wavelength calculated for various $P(E)_{intra}$, for temperature $T = 10\text{ K}$ and $T = 320\text{ K}$; (b) simplified configurational coordinate diagram of the system. Here the section along the parallel configuration coordinate is presented. Perpendicular vibrations are perpendicular to the figure surface. Radiative transitions are indicated by dashed arrows, non-radiative ones by solid arrows.

2E and 2T_2 electronic manifolds are allowed by the spin-orbit interaction. Thus, the frequency factor, $\tau_0^{-1} = (2\pi/\hbar)\xi^2/\hbar\omega$, where ξ is the spin-orbit matrix element and $\hbar\omega$ is the phonon energy (we have used $\tau_0^{-1} = 3 \times 10^{13}\text{ s}^{-1}$). $S^n(T)$ is the

Boltzmann occupation factor, and $|F_{eg}^{n-km-k'}|_{\parallel}$ and $|F_{eg}^{kk'}|_{\perp}$ are the absolute values of overlap integrals of the one-dimensional harmonic oscillator wave functions related to the parallel and perpendicular modes, respectively (see Fig. 1(b)). The probability of radiative transition has been assumed to be equal to $0.26 \times 10^6\text{ s}^{-1}$ (the inverse of the radiative decaytime). We have assumed that $P(E)_{intra}^k = P(E)_{intra}$, for all k , and we treat them as a free parameter of the model. Calculations have been performed using $P(E)_{intra}$ equal to 10^{15} s^{-1} , 10^{14} s^{-1} and 10^{13} s^{-1} . The results are presented in Fig. 1(a). For λ smaller than $\lambda_{nr} = 480\text{ nm}$ η_R^{Ti} starts to decrease, and its slope depends on the value of $P(E)_{intra}$. This decrease is because the probability of internal conversion to the 2T_2 electronic manifold, $P(E \rightarrow T)_{inter}^{ij}$, increases with n and becomes comparable to $P(E)_{intra}$ when the Ti^{3+} ion is excited above the energy barrier for non-radiative transitions, E_{nr} (the cross-over energy between the excited and ground electronic manifolds, see Fig. 1(b)). In our case $E_{nr} = 4507\text{ cm}^{-1}$ above the energy minimum of the 2E electronic manifold. One notices two regions of excitation. For $\lambda > \lambda_{nr}$ the quantum yield is determined by the slow radiative and non-radiative processes in the thermalized system, whereas for $\lambda < \lambda_{nr}$ the fast non-radiative internal conversion dominates. In the former case η_R^{Ti} depends only on temperature, whereas in the latter it is also dependent on the energy of the exciting photons. It should be mentioned that in the framework of standard approach one considers the quantum yield of the system to be dependent only on temperature. This case is represented by dashed lines obtained from our model by applying the a priori assumption

$$\frac{P(E)_{intra}^k}{P(E \rightarrow T)_{inter}^{kl} + P(E)_{intra}^k} = 1$$

for any l and k .

3. Analysis of photopyroelectric spectrum

The photopyroelectric spectrum of $Al_2O_3 : Ti^{3+}$ has been obtained using a novel non-contact photopyroelectric spectrometer, which allows

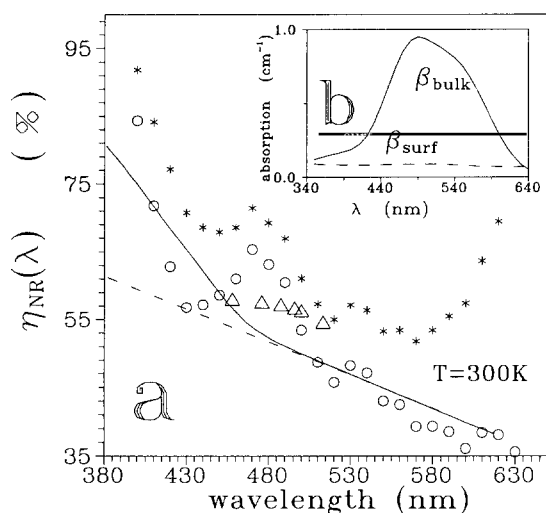


Fig. 2. (a) Non-radiative energy conversion efficiency for Ti^{3+} :sapphire. Asterisks corresponds to the total η_{NR} , obtained from the photopyroelectric spectrum of the sample; circles correspond to the non-radiative energy conversion efficiency of titanium ion; solid curve and dashed line correspond to $\eta_{\text{NR}}^{\text{Ti}}(\lambda, T)$ calculated according to Eq. (5) using $\eta_{\text{R}}^{\text{Ti}}$ given by Eq. (2) and $\eta_{\text{R}}^{\text{Ti}}$ independent of λ , respectively. Triangles correspond to η_{NR} of $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ obtained by Li et al. [7]. (b) Bulk and surface absorption of $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ system.

measurement of the absolute value of non-radiative energy transfer efficiency, $\eta_{\text{NR}}(\lambda, T)$, via a lock-in technique (for the experimental details see Ref. [5]). The experimental η_{NR} as measured, is presented in Fig. 2(a) (asterisks). It should be mentioned here that since we have the background absorption, related to the surface states, the η_{NR} obtained is related to the Ti^{3+} ions as well as to surface defects. Especially the large $\eta_{\text{NR}}(\lambda, T)$, for $\lambda > 620$ nm, is due to completely non-radiative de-excitation of surface defects. Knowing the contributions from the surface and the bulk crystal to the absorption spectrum (see Fig. 2(b)), one extracts $\eta_{\text{NR}}^{\text{Ti}}(\lambda, T)$ (circles in Fig. 2(a)) from η_{NR} , assuming that the non-radiative energy transfer efficiency related to the surface states is 100%. One analyzes

$\eta_{\text{NR}}^{\text{Ti}}(\lambda, T)$ using the relation [6]

$$\eta_{\text{NR}}^{\text{Ti}}(\lambda, T) = 1 - \eta_{\text{R}}^{\text{Ti}}(\lambda, T) \frac{\lambda}{\lambda_t}, \quad (5)$$

where λ and λ_t are the wavelengths of exciting and emitted photons, respectively, and $\eta_{\text{R}}^{\text{Ti}}(\lambda, T)$ is given by Eq. (2). Using $P(E)_{\text{intra}} = 2 \times 10^{14} \text{ s}^{-1}$, we were able to reproduce the $\eta_{\text{NR}}^{\text{Ti}}(\lambda, T)$ quite well (solid curve in Fig. 2(a)). The standard approach (η_{R} independent on λ) results in the dashed line in Fig. 2(a). It is seen that in the case of Ti^{3+} the large electron lattice coupling results in the increase of the probability of non-radiative inter-configurational internal conversion transitions for a highly excited system. For the exciting $\lambda < \lambda_{\text{nr}}$ this process competes with the intra-configurational non-radiative transitions and therefore results in an additional increase of $\eta_{\text{NR}}^{\text{Ti}}$.

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