Photoacoustic spectroscopy of YAG crystals doped with Ce

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Abstract

The absorption, luminescence and photoacoustic spectra of YAG:Ce\textsuperscript{3+} have been measured and analysed. Considering the photoacoustic and absorption spectra one has shown a decrease of the quantum efficiency of the Ce\textsuperscript{3+} below 90\% when luminescence is excited in the UV region. Simulation of the kinetics of nonradiative processes in the excited states of Ce\textsuperscript{3+} and hot luminescence has been performed. The Jahn–Teller type coupling in the excited states of Ce\textsuperscript{3+} has been evidenced.

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1. Introduction

Electronic structure and optical properties of the Ce\textsuperscript{3+} ions in Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (YAG) crystal are determined by the 4f- and 5d-electronic levels split by the spin-orbit interaction and the crystal field of $D_2$ symmetry. One observes the broad double band green–yellow luminescence and five broad absorption bands, related to 4f–5d transitions. The purpose of this paper is to analyse the nonradiative processes in the excited states of the Ce\textsuperscript{3+} ion and quantum efficiency of the system. We have at our disposal YAG monocrystals doped with Ce of a concentration between 0.05 and 0.2\%. The details concerning the material preparations are described elsewhere [1,2]. In this paper we present the optical and photoacoustic (PA) spectra of YAG with high concentration of Ce (0.2\%). We have analysed the standard spectroscopy (emission absorption spectra), and photoacoustic spectra of the material. The interpretation of standard spectroscopy experiments allowed us to calculate the parameters of the configurational coordinate diagram describing the energetic structure of the system. Then we modelled the nonradiative processes in the excited states of Ce\textsuperscript{3+}. Our calculation yields the conclusion that the homogeneous broadening of the absorption bands are related to the coupling of the system in the d\textsubscript{1} and d\textsubscript{2} states to the local lattice vibrations of various symmetry.

2. Experimental method

The PA signal results from generation of alternate heat flux in a sample, which is optically excited by a chopped beam of light. The periodical heat flux causes periodical changes of the sample surface temperature and in consequence the overpressure in gas filling the photoacoustic chamber. The investigated samples were $l_s=1$ mm thick plates so they could be regarded as thermally thick ($l_s \gg \mu$, where thermal diffusion length is given by the expression: $\mu = 1/a_\mu$, where $a_\mu$ is a thermal diffusivity of the sample and $a_\mu$ is a frequency of excitation modulation). For this case, according to the Rosenwaig–Gersho theory [3], improved by MacDonald et al. [4], following expression for pressure changes in the photoacoustic cell can be derived:

$$P = -\frac{i\gamma \cdot l_s \cdot P_0}{2\omega_\mu \cdot l_s \rho C_p} \left( \frac{\beta}{\sigma T_0 (g + 1)(r + 1)} \right) \beta_r \left[ 1 - \exp(-\beta \cdot l_s) \right].$$ (1)

Here $P$ is the complex signal amplitude, $I_0$ is the incident light intensity, $P_0$ and $T_0$ are the ambient pressure and temperature, respectively, $\gamma = C_p / C_v$ is the ratio of the
specific heats of the samples, \( \ell_g \) is the thickness of the gas layer in the photoacoustic cell, \( \beta, \rho \) and \( \beta_r \) are absorption, density thermal and expansion coefficient of the sample, respectively; \( g, r \) and \( \sigma \) are the complex parameters:

\[
g = \frac{k_\rho}{k_\beta} a_{\beta} r = (1 - i) \frac{\beta}{2a_\beta}, \sigma = (1 + i)a_\beta
\]

(2)

where \( k_\beta, k_\rho \) and \( a_\beta, a_\rho \) denote the thermal conductivity and thermal diffusivity for gas and the sample, respectively.

In the original models [3,4] it is assumed that one deals only with instantaneous and pure nonradiative transitions. In order to account for the existence of radiative transitions, the expression (1) should be modified by the factor \( \eta = Q/h\Omega \) where \( Q \) is the amount of the heat generated in the sample excited by a photon of energy \( h\Omega \). Usually the thermal expansion coefficient and sample thickness is small enough to neglect the second term in the parentheses of Eq. (1). In such a way the measured photoacoustic amplitude may be described by the following simplified relation:

\[
P = A \cdot I_0(h\Omega) \cdot \eta(h\Omega) \cdot \beta(h\Omega).
\]

(3)

Here the coefficient \( A \) is an apparatus factor independent of the excitation energy. In order to account for spectral characteristics of a light source, \( I_0(h\Omega) \), the sample spectrum is calibrated with a blackbody reference spectrum. Thus the quantity that is considered as PA signal from the sample is

\[
P_{\text{pas}} = A \cdot \eta(h\Omega) \cdot \beta(h\Omega).
\]

(4)

The PA spectra were carried out with 1 nm step in the wavelength range 270 to 550 nm using an SPM2 monochromator. The photoacoustic cell used was of a transmission type and was equipped with a 1/2-inch condenser microphone SV02 assembled to the SV01 preamplifier (Svantek, Poland). The Stanford Research, dual phase SR 850 lock-in amplifier driven by a computer was used for the signal registration and data acquisition. The modulation frequency 42 Hz was chosen for registration of the PA spectra. All PA spectra were calibrated with a carbon black reference. The measurements were taken at room temperature. Experimentally determined thermal diffusivity of YAG monocrystals is about 3.6×10\(^{-2}\) cm\(^2\)/s [5]. For the modulation frequency used, \( \omega = 42 \) Hz, this corresponds to the depth of sample penetration \( \mu = 1.6 \times 10^{-2} \) cm. As for the whole range of photon energies the sample absorption coefficient \( \beta \) does not exceed the value of 30 cm\(^{-1}\), the condition for photoacoustic signal nonsaturation: \( \beta \mu < 1 \) was fulfilled in this spectral range. Luminescence was excited by a xenon lamp and detected with an SPM2 monochromator and photomultiplier. Absorption was measured by a standard Specord photometer. All equipment was controlled by a computer.

3. Configuration coordinate diagram of the Ce\(^{3+}\)

To obtain the configuration coordinate diagram of the Ce\(^{3+}\) system besides the photoacoustic spectra, the absorption and emission spectra have been measured. All spectra are presented in Fig. 1. The double band seen in the emission spectra is related to \( ^2F_{5/2} \leftrightarrow ^2F_{7/2} \) ground state splitting. One can see that the photoacoustic spectrum reveals evident structure related to the f\(\rightarrow\)d internal transition in the Ce\(^{3+}\) ion, indicated as \( d_1, d_2, d_3 \) and \( d_4 \).

Whereas the \( d_1 \) and \( d_2 \) bands are very similar in the absorption and photoacoustic spectra the \( d_3 \) and \( d_4 \) bands are much better seen by the photoacoustic method. We have related this effect to decrease of the quantum efficiency of the Ce\(^{3+}\) system when it is excited to the \( d \) states. For analysis of the energetic structure of the Ce\(^{3+}\) ion we have considered also the hot luminescence related to \( d \rightarrow ^2F_{5/2} \leftrightarrow ^2F_{7/2} \) transitions, measured by Suzuki et al. [6]. Since we have not measured the hot luminescence ourselves we have not indicated them in Fig. 1.

The structure seen in the absorption at the region of 40,000–50,000 cm\(^{-1}\) is probably related to creation bound excitons. The P A spectra were carried out with 1 nm step in the wavelength range 270 to 550 nm using an SPM2 monochromator. The photoacoustic cell used was of a transmission type and was equipped with a 1/2-inch condenser microphone SV02 assembled to the SV01 preamplifier (Svantek, Poland). The Stanford Research, dual phase SR 850 lock-in amplifier driven by a computer was used for the signal registration and data acquisition. The modulation frequency 42 Hz was chosen for registration of the PA spectra. All PA spectra were calibrated with a carbon black reference. The measurements were taken at room temperature. Experimentally determined thermal diffusivity of YAG monocrystals is about 3.6×10\(^{-2}\) cm\(^2\)/s [5]. For the modulation frequency used, \( \omega = 42 \) Hz, this corresponds to the depth of sample penetration \( \mu = 1.6 \times 10^{-2} \) cm. As for the whole range of photon energies the sample absorption coefficient \( \beta \) does not exceed the value of 30 cm\(^{-1}\), the condition for photoacoustic signal nonsaturation: \( \beta \mu < 1 \) was fulfilled in this spectral range. Luminescence was excited by a xenon lamp and detected with an SPM2 monochromator and photomultiplier. Absorption was measured by a standard Specord photometer. All equipment was controlled by a computer.
4. The nonradiative processes

Considering the photoacoustic and absorption spectra one can get the information about relative quantum efficiency of the system. Specifically the quantity that can be calculated is relative efficiency of the nonradiative processes (the heat emitted per single absorbed photon):

$$\eta(h\Omega) \propto \frac{P_{\text{pas}}(h\Omega)}{\beta(h\Omega)}.$$  \hspace{1cm} (5)

Here $P_{\text{pas}}$ is given by (4). Unfortunately we have not measured the photoacoustic and absorption spectra using the same spectrometer. This is a reason why, to avoid the errors related to apparatus spectral resolution, we have considered the integrated absorption and photoacoustic signal. Thus we have estimated relative efficiency of the nonradiative process under particular excitation $h\Omega_k$ using the relation:

$$\eta(h\Omega_k) \propto \frac{\int d\Omega P_{\text{pas}}(h\Omega)}{\int d\Omega \beta(h\Omega)}.$$  \hspace{1cm} (6)

Here $2\Omega_0$ is the integration range, which should extend over the whole single band. In such a way one obtains the ‘experimental efficiency’ for several excitation energies. We have performed calculations dividing all spectra into three parts. The first corresponds to the $d_1$ band, the second corresponds to the $d_2$ band and the third corresponds to the $d_1$ and $d_2$ bands. The results are presented in Fig. 3. It is seen that the heat emitted per one absorbed photon increases with the excitation energy. One can assume that only nonradiative processes take place during the thermalization of the system in the excited electronic manifold. Under this approximation one obtains the dependence of quantum efficiency on excitation energy given by:

$$\eta(h\Omega) = \frac{h\Omega - h\Omega_{\text{lum}}}{h\Omega}.$$  \hspace{1cm} (7)

where $h\Omega_{\text{lum}}$ is the energy of the maximum luminescence band. We have taken $h\Omega_{\text{lum}} = 17,314$ cm$^{-1}$ from the first moment of the emission lineshape. If the formula (7) is valid it means that after excitation the system relaxes nonradiatively to the $d_1$ state from which only the radiative deexcitation is possible. Thus, although the system emits heat its quantum efficiency is still equal to unity. The dashed line in Fig. 3 corresponds to the theoretical nonradiative transition efficiency calculated according to (7). It is easy to see that experimental $\eta$ increases with energy much faster than it is predicted by formula (7). This is a reason one has to consider also the internal conversion nonradiative transitions between the excited

![Diagram](image-url)
and ground electronic manifolds that take place during as well as after thermalization in the metastable state. When these processes are taken into account the heat emitted per photon is given by the following more complicated formula:

\[ \eta(h\Omega) = \frac{h\Omega - h\Omega_{\text{num}} + \theta(h\Omega - h\Omega_{\text{num}}) \cdot h\Omega_{\text{num}} + \vartheta \cdot h\Omega_{\text{num}}}{h\Omega} \]  

(8)

Here \( \theta(h\Omega - h\Omega_{\text{num}}) \) is the probability of the internal conversion from the excited to the ground electronic manifold that takes place before thermalization of the system in the metastable excited state (the fast processes) and \( \vartheta \) is the probability of the nonradiative processes in the metastable state (the slow process). Detailed description of the kinetics of the fast and slow nonradiative processes is given in Ref. [7]. Since the probability of the fast internal conversion usually increases with energy of the excitation [7], we consider this process as responsible for steeper rise of the experimental nonradiative transitions efficiency. Assuming \( \vartheta = 0 \) one obtains \( \theta_{d_2}(32,000 \text{ cm}^{-1}) = 0.075 \) and \( \theta_{d_2,d_4}(37,800 \text{ cm}^{-1}) = 0.14 \). One has to notice that under assumption \( \theta = 0 \), the non-zero \( \vartheta \) yields slower rise of \( \eta_1 \) than \( \eta \).

5. Analysis of the hot luminescence

Having the configurational coordinate diagram one can consider the intensity and the kinetics of the hot luminescence, the radiative transition from the d excited state to the \( ^3\text{F} \) ground state (see Ref. [6] and Fig. 2). The hot luminescence lineshape, that is very similar to the ordinary luminescence \( (d \rightarrow F_{5/2} \rightarrow F_{7/2}) \) lineshape suggests that the d state has to be also the metastable state. It means that the excited system has enough time in the zero-phonon state of the d electronic manifold to decay radiatively through \( d \rightarrow 4f(F_{5/2} \rightarrow F_{7/2}) \) transition. On the other hand the intensity of the hot luminescence is about 1000 times weaker than ordinary luminescence, also the hot luminescence decay time is only in the 40 ps range [6]. Both these facts evidence that the dominating process in the d state is the nonradiative internal conversion to the d electronic manifold. Considering the configurational coordinate diagram presented in Fig. 2 one can see that the crossing of the d and d electronic manifolds appears exactly in the minimum energy of the d state. It is not evident that in the system the lifetime of the zero-phonon level of the d state is long enough to yield the hot luminescence of the respective lineshape. This is a reason why we consider the deexcitation processes in the d and d states more carefully.

The radiative deexcitation rate of the system occupying the d state, \( P_{d_2} \), is given by following relation:

\[ P_{d_2}(T) = \frac{P_{d_2}^{\text{rad}}}{P_{d_2}^{\text{rad}} + P_{d_2}^{\text{nonrad}}(T)} \]  

(9)

where \( T \) is temperature, \( P_{d_2}^{\text{rad}} \) is a probability of the radiative \( d_2 \rightarrow 4f(F_{5/2} \rightarrow F_{7/2}) \) transition, and \( P_{d_2}^{\text{nonrad}}(T) \) is the temperature dependent probability of the nonradiative process given by

\[ P_{d_2}^{\text{nonrad}}(T) = \sum_n e^{-\frac{n\hbar\omega}{kT}} W_{nm}^{\text{num}}. \]  

(10)

The probability of the internal conversion between particular vibronic states is given by

\[ W_{nm}^{\text{num}} = f \cdot \left| \int \chi_m(Q) \chi_n(Q) \right|^2 \cdot \delta(E_m - E_n). \]  

(11)

The quantity \( f \) is called the frequency factor and describes the mixing of the electronic part of the wave functions of the system in d_1 and d_2 states [8]. Radiative transition rate \( P_{d_2}^{\text{rad}} \) can be estimated if the probability of the radiative transition from the d_1 state to the ground state, \( P_{d_1}^{\text{rad}} \), is known. Considering that radiative transitions...
between the $d_2$ and $d_1$ states and the ground state are of the same type, one calculates $P_2^{\text{rad}} = P_1^{\text{rad}} (\hbar \Omega_2 / \hbar \Omega_1)^3$ where $\hbar \Omega_2$ and $\hbar \Omega_1$ are energies of respective photons. Using $\hbar \Omega_2 = 25,730 \text{ cm}^{-1}$ [6], $\hbar \Omega_1 = 17,314 \text{ cm}^{-1}$ and $P_1^{\text{rad}} = 15 \times 10^9 \text{ s}^{-1}$ [2] one obtains $P_2^{\text{rad}} = 5 \times 10^{17} \text{ s}^{-1}$. The frequency factor is related to the type of interaction between initial and final electronic states, given by respective matrix elements $H_{12}$

$$f = \frac{2\pi H_{12}^2}{\hbar \omega}.$$ (12)

Assuming that the mixing is caused by the spin-orbit interaction one obtains $f \approx 3 \times 10^{13} \text{ s}^{-1}$ [9]. Finally one can calculate the dependence of the hot luminescence decay time on temperature from the relation $\tau_\phi(T) = 1 / (P_\phi(T))$. We have considered the data listed above as reliable, therefore we have performed calculations of the hot luminescence kinetics in the YAG:Ce$^{3+}$ system using the relative electron–lattice coupling energy, $S_{12} h \omega$, taken as the only free parameter of the model. The overlap integrals were calculated using the harmonic oscillator wave functions describing the vibrations in the $d_1$ and $d_2$ states. The squares of the overlap integrals between the $d_2$, $d_1$ oscillation wave functions, for different relative electron–lattice coupling strengths are presented in Fig. 4a. The respective configuration coordinate diagrams are presented in Fig. 4b. One should notice that the vibronic overlap integrals depend only on the electron lattice coupling energy and phonon energy, so the curves presented in Fig. 4a are quite universal. It is easy to find that using the radiative transitions rate and the frequency factor listed above with the strength of the electron–lattice coupling as it is presented in Fig. 2 we cannot get the effective hot luminescence even so weak as it has been measured [6].

For the electron–lattice coupling equal to 8000 cm$^{-1}$ we have obtained the lifetime of the $d_2$ state approximately equal to $10^{-13}$ s instead of the measured hot luminescence lifetime that is about 40 ps [6]. Moreover the vibronic overlap integral is already the largest in the $d_2$ zero-phonon state. In such a case if the hot luminescence takes place their lifetime does not depend on temperature. To get the decrease of the hot luminescence lifetime with temperature we need significant increasing of vibronic overlap integrals in the excited phonon states with respect to the zero-phonon state. This suggests much weaker relative electron–lattice coupling between $d_1$ and $d_2$ than has been detected from consideration only of the fully symmetrical lattice mode. Actually the best fit of the calculated dependence of the hot luminescence decay time on temperature to the experiment has been obtained for the effective electron–lattice coupling $S_{12} h \omega = 4500–4750 \text{ cm}^{-1}$ (see Fig. 5).

The inconsistency in estimations of the electron–lattice interaction energy in the excited states of the Ce$^{3+}$ ion can be explained by the effect of the coupling of excited states to the non-symmetrical vibration modes. One considers that $d_2$ and $d_1$ states are in fact the components of the $d$ orbital occupied by a single electron. Actually other $d_1$ systems (like Ti$^{3+}$ V$^{4+}$) manifest usually the Jahn–Teller effect [10,11]. We expect the same in the $d_1$ $d_2$ states in the case of Ce$^{3+}$. Actually since $d_1$ and $d_2$ states are probably not degenerated one does not have to deal with typical Jahn–Teller effect, but still one can consider the effect as a coupling to the Jahn–Teller mode. The new mode can be described by a single effective configuration coordinate $Q_{J = 1}$, which has to be orthogonal to the coordinate $Q_{A_2}$ describing the breathing mode [12]. Using $S_1 h \omega = 2225$
cm$^{-1}$, $S_1\hbar\omega = 1785$ cm$^{-1}$ and $S_2\hbar\omega = 4675$ cm$^{-1}$ one can calculate the contribution from the Jahn–Teller coupling to the total electron–lattice coupling in particular states. Let us analyse the possible positions of the minimums energy of the ground and $d_1$ and $d_2$ excited states in the two-dimensional configurational coordinate space (see Fig. 6a). Fortunately the ground state is the $f$ state which is not coupled to the lattice. This is a reason that the positions of the minimums energy of the $d_1$ and $d_2$ excited states can be unambiguously represented in the two-dimensional configuration space by their distances from the minimum of the ground state. Since the distance between $d_1$ and $d_2$ minimums is constants, all positions form the triangle that is fixed in the (0,0) point. The spectroscopic data will not change when the ‘triangle’ is rotated around the (0,0) point, although the angle of rotation changes the distribution of the electron–lattice coupling energy between the coupling to the breathing.
mode and Jahn–Teller mode in each individual excited state. One defines these energies as $E_{A_1} = Q_{A_1}^2/2$ and $E_{I-T} = Q_{I-T}^2/2$, respectively. Calculated contributions from the coupling to the Jahn–Teller mode, the energies $E_{I-T}(d_1)$, $E_{I-T}(d_2)$ and $E_{I-T}(d_1, d_2)$ are presented in Fig. 6b. Actually we do not know the contributions from the Jahn–Teller coupling to the electron–lattice interaction energy in the individual states. In Fig. 6b it is seen that these contributions can extend over the full energy range. However the quantity $E_{I-T}(d_1) + E_{I-T}(d_2)$ that is a sum of the Jahn–Teller coupling energies in the excited states is more stable. This effect can be considered as a proof of existence of the Jahn–Teller type coupling in the excited states of the Ce$^{3+}$ ion.

6. Conclusions

We have presented the absorption, emission and photoacoustic spectra of the YAG:Ce$^{3+}$ system. Based on these data we have obtained the energetic structure of the Ce$^{3+}$ system in the form of the configuration coordinate diagram. Detailed analysis of the kinetics of the radiative and nonradiative processes in the excited states has shown that the single-dimensional configuration coordinate diagram cannot represent the proper structure of the excited $d_1$ and $d_2$ states. We need also to consider a coupling of the system to the Jahn–Teller type mode. Considering the absorption and photoacoustic spectra we have shown a decrease of quantum efficiency of the Ce$^{3+}$ from 1 to 0.85 when the system is excited in the UV region by $d_3$ and $d_4$ states.

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