

ON DETERMINATION OF QUANTUM EFFICIENCY OF DE-EXCITATION PROCESSES OF IONS IN CRYSTAL MATRICES FROM PHOTOACOUSTIC MEASUREMENTS

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ABSTRACT

Investigations of photo acoustic spectra (PAS) of transition metal ions in crystal matrices (e.g. $Y_3Al_5O_{12}$ (YAG) doped with Cr^{4+} and Cr^{3+} were performed to analyse quantum efficiencies of radiative (R) and non-radiative (NR) processes. Relations between PAS and optical absorption spectra (OAS) allow directly to get information about participation of R and NR processes in relaxing of the excitation energy. Further measurements of the dependences of phase shift between PA signal and optical excitation against light modulation frequency have been compared with theoretical predictions.

INTRODUCTION

Photoacoustic spectroscopy (PAS) applied in parallel with standard optical spectroscopy (OS) methods enables quantitative examinations of non-radiative (NR) relaxation processes in luminescent centres situated in the crystal lattice [1]. For example Cr^{3+} or Cr^{4+} excited ion in $Y_3Al_5O_{12}$ (YAG) crystal being such a centre surrounded by other atoms of the lattice represents a specific system of energy electron levels splitted by the crystal field of a given symmetry and by spin-orbital interaction. Though the system of energy levels is very complicated, the kinetics of relaxation processes of ion excitation takes place according to the Jablonski scheme by radiative (R) and non-radiative (NR) transitions. In systems where the strong coupling between excited ion and the crystal exists the NR processes play an essential role decreasing the quantum efficiency of the systems.

NR transitions present an additional mechanism of the excitation relaxation (i.e. deexcitation process) of luminescent centres usually competitive to the R ones (emission of photons). The NR relaxation is associated with the emission of a cascade of phonons and as a consequence the thermal and acoustic energy is generated. Detection of this energy in photoacoustic (PA) signal is a good way for experimental examination of NR processes.

The theoretical model proposed by Grinberg and Mandelis [2,3] and next extended by Grinberg and Jaskolski [4] has been used for interpretation of our results and for elaboration of the new model describing the kinetics in strongly luminescing crystals taking into account an additional NR transfer of excitation energy from the luminescent centre towards the surface states [5,6].

In this paper some considerations in respect to that model in the light of the measurement results including dependences of the phase shift between PA

signal and optical excitation against light modulation frequency, are presented and discussed.

SAMPLES AND MEASURING METHODS

The procedure of samples preparation of YAG crystals doped with Cr atoms (grown by the Czochralski method) and their high temperature annealing treatment as well as measuring methods for PAS and optical absorption spectra (OAS) have been described in [1]. Samples annealed in air contained mainly Cr^{4+} ions but annealed in hydrogen at 1200 °C for 10 h contained only Cr^{3+} ions.

OA and PA spectra were measured within 400 — 800 nm range. Amplitude and phase characteristics for PA signals against frequency of the excitation light were measured in the range of 20-200 Hz [1,7].

PA AND OA SPECTRA OF Cr^{3+} AND Cr^{4+} IONS IN YAG AND THE BULK TO SURFACE STATES DEEXCITATION MODEL.

NR processes in YAG crystals doped with Cr were examined depending on annealing treatments of the samples in which chromium atoms appeared in two charge states $3+$ or $4+$. A dominant role in depopulation of the excitation of Cr^{4+} ions (situated in tetrahedral surrounding in the lattice matrix) play NR processes of internal conversion between the first excited state and the ground one. In the case of Cr^{3+} ions (in octahedral coordination) the lowest excited state is a metastable one (of about 3-10 ms life-time) and therefore YAG crystals containing these high-pole Cr^{3+} ions are characterized by high excitation quantum efficiency.

In [1] PA and OA spectra were analysed. According to Grinberg and Mandelis model [2,3] developed by Grinberg and Jaskolski [4] the quantum efficiency of the system is described by

$$h_R(\mathbf{h}\Omega, T) = \left[\prod_{k=1}^{n(\mathbf{h}\Omega)} \frac{p_{\text{intra}}^k(e)}{p_{\text{intra}}^k(e) + p_{\text{inter}}^{kl}(e \rightarrow g)} \right] \left[\frac{p'_R}{p'_R + p'_{NR}(T)} \right] \quad (1)$$

where $p_{\text{intra}}^k(e)$ is the probability of NR transition between $k, k-1$ vibronic states of the electronic excited state (phonon emission), $p_{\text{inter}}^{kl}(e \rightarrow g)$ is the probability of NR internal conversion from the excited state before thermalization, p'_R, p'_{NR} are, respectively, probability of photon emission and probability of NR relaxation in metastable excited state after thermalization; $\mathbf{h}\omega$ is the excitation energy.

Next, according to Rosencweig and Gersho theory [8] the PA signal should be proportional to the light absorption coefficient β and to the efficiency of the transfer process of the excitation energy into heat $h_{NR} = 1 - h_R$ so

$$PAS \propto b \cdot h_{NR} \quad (2)$$

According to (1) and (2) one should expect that the quantum efficiency of the system would decreased with increasing of excitation energy. The ratio of PAS to OAS (or β) should increase against increasing of excitation energy.

Fig.1 presents comparisons between OAS and PAS for examined YAG:Cr crystals. One can see that for the cases of Cr^{4+} ions domination (Fig.1a and 1b) the PAS overlaps OAS. That confirms the fact that in whole spectral range a very effective process of excitation energy into heat transfer takes place, so $\eta_R=0, \eta_{NR}=1$. On the other hand for the case of the sample containing only Cr^{3+} ions (Fig.1c) the ratio of PAS/OAS decreases with increasing of the excitation energy. According to the Rosencweig-Gersho model that would indicated that the quantum efficiency increased in the range of the higher energy excitation. However, according to the Grinberg-Mandelis model such tendency is not possible for an isolated centre. In conclusion we have postulated that for increasing of the relative PA signal a transportation mechanism of excitation energy from the centre to the surface (where heat is released) is responsible. Existing of the metastable state 2E of the excited ion Cr^{3+} provide for such mechanism.

We have elaborated the bulk-to-surface states deexcitation model and described in [5,6] and we have established a new relation between PA signal and OA coefficient $\beta(E)$

$$Q_{PAS} \propto b(E) \sqrt{\left[\frac{E - E_m}{E} + \text{Re}(K) \frac{E_m}{E} \right]^2 + \left[\text{Im}(K) \frac{E_m}{E} \right]^2} \quad (3)$$

where w is modulation frequency of the excitation, S_2 is the inverse of thermal diffusivity length; $\text{Re}(K), \text{Im}(K)$ are the real and imaginary parts of K , respectively;

τ_m is defined by $1/\tau_m = 1/\tau_R + 1/\tau_{NR}$, where τ_R and τ_{NR} are radiative and non-radiative life times

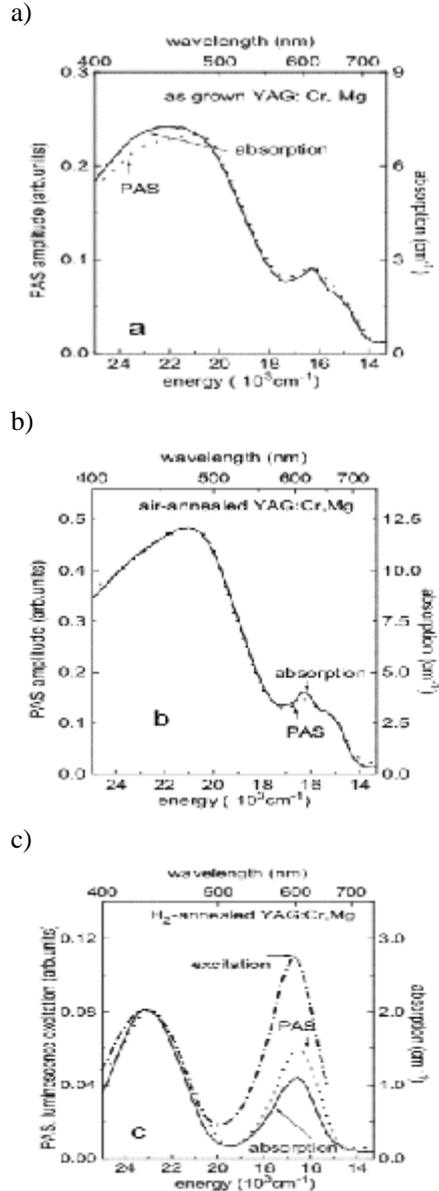


Fig.1 PA and OA spectra of YAG:Cr : as grown (a), annealed in air (b) and annealed in hydrogen (c); also, in (c) the spectrum of excitation of emission is presented.

K function can be expressed as

$$K = P_{NR}^e(E) + (1 - P_{NR}^e) \cdot P_{NR}^m \cdot \frac{(1 + e^{-s_2 L}) e^{-i\sqrt{w}}}{\sqrt{1 + w^2 t_m^2}} + (1 - P_{NR}^e) K_0 \sqrt{w} \frac{(1 + e^{-s_2 L}) e^{-i(\sqrt{w} - \frac{p}{4})}}{\sqrt{1 + w^2 t_m^2}} \quad (4)$$

the coefficient K_0 is related to the maximal distance for the transportation of excitation energy and to the thermal diffusivity constant a_2 by the following expression

$$K_0 = \frac{R}{5\sqrt{2a_2}} \left[\frac{1}{p} + \frac{p^2}{4} \right] \quad (5)$$

R is the radius of diffusion of excitation energy.

It is easy to see that for a great R, K may be larger than 1. In consequence that may cause decreasing of the ratio $Q_{PAS}(E)/\beta(E)$ with increasing of excitation energy what has been observed in [1] for the YAG:Cr³⁺ system and is presented in Fig 1c.

For the special YAG:Cr³⁺ system where exist two spectral bands corresponding to transitions $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_{1a}$ we used for the analysis the following quantity

$$g = \frac{Q_{PAS}(^4A_2 \rightarrow ^4T_{1a})}{b(^4A_2 \rightarrow ^4T_{1a})} \cdot \frac{b(^4A_2 \rightarrow ^4T_2)}{Q_{PAS}(^4A_2 \rightarrow ^4T_2)} \quad (6)$$

Fig.2 presents the dependence of γ against modulation frequency of the light excitation beam. Experimental data (black triangles) are between 0.5-0.6. The calculated values of γ using (3) and (4) for several values of K_0 are given for comparison.

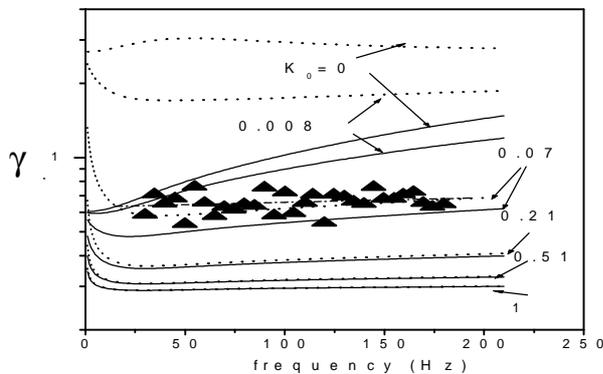


Fig.2. Dependence of γ against modulation frequency of exciting light for YAG:Cr³⁺

The analysis of spectra and calculated results allowed to establish that the probability of transition P_{NR} is equal 0 and 0.63, respectively, for the excitation through transitions $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_{1a}$. In further calculations K_0 and P_{NR} were treated as fitting parameters. The dotted curves in Fig.2 correspond to the data assuming that there in Cr³⁺ the internal conversion do not take place after thermalization of the state $^2E (P_{NR}=0)$ but the solid curves at the assumption that the NR internal conversion is dominating ($P_{NR}=1$). In fact the quantity γ is determined by two effects: migration of excitation energy to the surface and dependence of probability of the fast NR internal conversion process P_{NR} on the excitation energy.

PAS PHASE CHARACTERISTICS IN Cr³⁺ AND Cr⁴⁺ CENTRES IN YAG CRYSTAL MATRICES.

Results of PAS phase characteristics against modulation frequency were obtained by A.Sikorska and presented in [7]. Again samples of YAG:Cr annealed in air and in hydrogen were examined. For each of the samples the phase characteristics were experimentally determined for two wavelengths of exciting light corresponding to the maxima of absorption spectral bands. Next, they were compared with the calculated ones basing on the classical PA model or on the extended model including migration of excitation energy to the surface of a sample [5,6]. From the classical model one can get following expression for the phase delay of the PA signal assuming a thermally thick sample [6,7,9] and considering a three-levels system

$$j = -p + \text{arctg}(bm+1) - \text{arctg} \left\{ \frac{wt}{1 + \frac{Q_e}{Q_m h_{NR}} [1 + (wt_m)^2]} \right\} \quad (7)$$

where τ_m is the life-time of the metastable level, Q_e and Q_m are, respectively, fast and slow heat components determined per one molecule, h_{NR} is the quantum efficiency of light energy into heat conversion $h_R = 1 - h_{NR}$ is quantum efficiency of the radiative transition.

In Fig.3 the phase characteristics are presented for the YAG:Cr⁴⁺ (a) and YAG:Cr³⁺ (b) samples. For the Cr⁴⁺ case (Fig.3a) the dependence reflects directly relations corresponding to the values of absorption coefficient and the life-time of the excited level and is in agreement with the classical model. For the Cr³⁺ case (Fig.3b) interpretation has been performed using the extended theoretical model (formulae (3) and (4)) taking into account excitation energy migration effect. This model allows to foresee the phase jump of the value $\pi/4$ (in respect to the classical model) appearing in expression (4) and visible in Fig.3b. The phase jump is associated with the NR deexcitation of the excitation energy through the surface states. The analysis of frequency phase characteristics for different values of excitation energy corresponding to different absorption spectral bands also allowed to explain changes of the mutual position of the experimental dependences for the corresponding short- and long-wave bands in Cr⁴⁺ and Cr³⁺ (Fig.3)[7]. According to results of the paper [4] it was shown that for YAG:Cr³⁺ system radiation quantum efficiency should decrease with decreasing of the wavelength of excitation. For the excitation at 438 nm it should be (for arbitrary concentration of chromium) much lower than for the excitation at 600 nm. The effect has been illustrated in [7] by the

theoretical diagram of phase shift characteristics calculated for 438 and 600 nm. Comparing experimental characteristics with the diagram curves one can evaluate the quantum efficiency related to the excitation for a sample at a given absorption band.

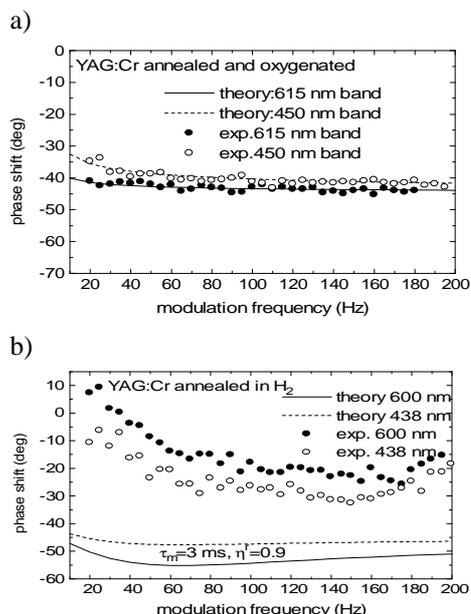


Fig.3 Dependences of PA signal phase shift against light modulation frequency for YAG:Cr⁴⁺ (a) and for YAG:Cr³⁺ (b).

CONCLUSIONS

Examinations of NR relaxation processes in YAG:Cr⁴⁺ and YAG:Cr³⁺ have shown that these two systems represent two model types for those processes. The first one corresponds to very effective transfer of excitation energy into heat: $\eta_R=0$ and $\eta_{NR}=1$ in the whole spectral range. In this case PAS coincide with OAS (Fig.1b). The second one corresponds to the situation when the ratio of PA signal to OA coefficient was not constant and decreased with increasing of excitation energy (Fig.1c).

For systems for which proportionality between PAS and OAS takes place the Rosencweig-Gersho theory is valid. Relative quantum efficiency in characteristic spectral ranges can be determined as the ratio of PA signal to absorption coefficient according relation (2) where $h_{NR}=1-h_R$. In these cases the quantum efficiency η_R has been interpreted according to the Grinberg-Mandelis model.

For systems strongly light absorbing (of not so great ion concentration) one can use the classical Quaze-Poulet model [9] which takes into account in PA signal competitive NR processes of generation of fast and slow heat components related to corresponding life-times of excited levels (see expression (7)), however for greater ion concentration (above

$2 \cdot 10^{20}$ centres/cm³), for long life-time processes, one has to take into account possibility of migration of excitation energy to surface states and then the extended model (expressions (3) - (6)) can be used.

Important and useful information for determination of quantum efficiency provide PA signal phase shift characteristics against modulation frequency of the excitation light. Such characteristics measured for given spectral bands (438 and 600 nm for YAG:Cr) can be compared with calculated data either for classical model (expression (2)) or for the extended model (expressions (4) and (5)) (Fig.3). Next, the quantum efficiency can be evaluated by comparing results with the theoretical diagram of PAS phase shift dependences against modulation frequency constructed for different values of η_R for given bands of excitation energy [7].

ACKNOWLEDGMENTS

This paper is a summation report of several works performed within the Polish Committee for Scientific Research Grant No. 7T07B04918.

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