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A. Mandelis, J. Vanniasinkam, S. Buddhudu. Absolute non-radiative energy conversion efficiency spectra in $\text{Ti}^{3+} : \text{Al}_2\text{O}_3$ crystals measured by non-contact quadrature photopyroelectric spectroscopy. Journal de Physique IV Proceedings, 1994, 04 (C7), pp.C7-393-C7-396. 10.1051/jp4:1994792 . jpa-00253323

HAL Id: jpa-00253323

<https://hal.science/jpa-00253323>

Submitted on 1 Jan 1994

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Absolute non-radiative energy conversion efficiency spectra in $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystals measured by non-contact quadrature photopyroelectric spectroscopy

A. Mandelis, J. Vanniasinkam and S. Buddhudu

Photothermal and Optoelectronic Diagnostics Laboratory, Department of Mechanical Engineering, University of Toronto, Toronto, Canada, M5S 1A4

Photopyroelectric spectroscopy (PPES) was used in a novel non-contact experimental configuration to obtain, for the first time, high-resolution absolute spectra of the optical-to-thermal energy conversion efficiency (non-radiative coefficient), $\eta_{\text{NR}}(\lambda)$, of Ti: Sapphire laser crystals with widely different figures of merit. These spectra were found to depend on the optical quality of the bulk and of the polished surfaces of the Ti: Sapphire material.

I. INTRODUCTION

Dynamic frequency-domain photothermal-based methods, although attractive because they can be used single-ended and self-consistently for nonradiative quantum efficiency measurements, cannot be used with fast relaxing solid-state laser materials due to their limited dynamic range. On the other hand, combined photothermal and optical spectroscopy methods can be used without such limitations, yet they invariably lead to compromised measurement accuracy due to the increased number of experimental operations required by such independent methodologies, which must also include different calibration procedures. These procedures would be difficult, or impossible, to apply with high-quality optical materials, which only generate minute thermal-wave signals.

2. PHOTOPYROELECTRIC SPECTROMETER DESIGN

We modified our original photopyroelectric (PPE) spectrometer [1] to incorporate a variable thickness air layer between sample back-surface and polyvinylidene fluoride (PVDF) pyroelectric detector, to play the role of thickness-adjustable, truly transparent thermal-wave phase-shifter, which is also used as PVDF d.c. drift compensator *and* as thermal contact resistance eliminator, Figure 1. Furthermore, the lock-in quadrature signal was monitored, rather than the phase channel [2] in our experiments: it was found that the quadrature is more stable than the PPE phase, and thus more sensitive to minute signal changes by a factor of ~ 3 .

Fig. 1 Experimental geometry for the theoretical analysis of non-contact PPEs of a transparent sample of thickness L , optical absorption coefficient $\beta(\lambda)$, and nonradiative energy-conversion efficiency $\eta_{NR}(\lambda)$. Air layer thickness L ; semi-infinite PVDF detector. Optical modulation angular frequency: ω ; incident optical intensity I_0 .

To put the sensitivity of the new PPE spectrometer in perspective, Coufal measured PPE phase shifts in the $0.1\text{--}0.8^\circ$ range with fixed-thickness thermal-wave phase shifter with a *ca.* 0.1° phase resolution [2]. He was thus able to measure optical-to-thermal energy conversion efficiencies, η_{NR} , in the $0.55\text{--}0.9$ range. By comparison, our combined use of quadrature detection with an absorption-free highly controllable variable-thickness thermal-wave phase shifter (i.e. the air-gap layer) allowed monitoring of minute signals corresponding to phase-shifts in the $0.02\text{--}0.2^\circ$ range with 0.015° phase resolution. This order-of-magnitude improvement in sensitivity was crucial for the acquisition of entire Ti: Sapphire $\eta_{NR}(\lambda)$ spectra, owing to the high optical transparency and low $\eta_{NR}(\lambda)$ values ($< 20\%$) of the Ti: Sapphire laser crystals.

3. EXPERIMENT AND RESULTS

Ti: Sapphire crystals from Union Carbide were studied. The crystals were grown by the Czochralski pulling technique. Some samples were subjected to further annealing in pure H_2 at 1940°C for 180h yielding a much higher figure-of-merit ($\text{FOM} \approx 800$). Finally, all samples were subjected to "low temperature" annealing at 1100°C for 12h, following the "rough" fabrication (slicing and grinding).

Optical absorption coefficient, $\beta(\lambda)$, spectra were obtained from the PPE signal in the purely optical transmission (thick gas-layer) mode, Figure 2. These were subsequently used self-consistently in a developed phenomenological theoretical model [3] along with PPE signal quadrature spectra (purely thermal transmission, thin gas-layer mode), to extract $\eta_{NR}(\lambda)$ spectra, Figure 3. These spectra were found to depend on the optical quality of the bulk *and* of the polished surfaces of the Ti: Sapphire material.

4. DISCUSSION

The spectral lineshapes of the optical absorption coefficient, Fig. 2, are typical of the $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ system. These consist of a broad peak centered around 470 nm, which corresponds to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition broadened by phonons. The shoulder on the low-energy side is due to Jahn-Teller splitting of the 2E_g (upper) state[4]. The thick samples exhibit smooth absorption curves, with the absorption coefficient of the $\text{FOM} = 800$ sample somewhat lower. This is in agreement with previous observations, [5] which have established that annealed Ti: Sapphire samples exhibit lower absorption profiles, due to the reduction in certain kinds of point defects and the relaxation of Ti^{3+} from interstitial or defect sites in the desired Al^{3+} sites.

Fig. 2 Optical absorption spectra of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystals, obtained with PPES in the purely optical transmission mode, at $f = 9$ Hz. (Δ - Δ - Δ): $l = 0.0813$ cm, FOM = 40; ($\times$ - $\times$ - $\times$): $l = 0.1295$ cm, FOM = 800; (+-+-+): $l = 2.0169$ cm, FOM = 40; and ($\square$ - $\square$ - $\square$): $l = 2.0125$ cm, FOM = 800

Fig. 3 Optical-to-thermal energy conversion efficiency spectrum of a Ti:Sapphire FOM = 40 crystal

Preliminary attempts at identifying the origins of the $\eta_{\text{NR}}(\lambda)$ responses of the absorption band indicate a high degree of complexity below the metastable level absorption threshold. Following optical absorption and ${}^2T \rightarrow {}^2E$ electronic excitation, there should be fast nonradiative transitions (“fast heat”) to the long-lived metastable level with $\sim 3.3 - 3.8$ - μs lifetime at room temperature[5,6]. Between laser-active levels only heat governed by the nonradiative transition probability-quantum efficiency of the Ti^{3+} ion in the Al_2O_3 host should be released (“slow heat”). On the time scale of our modulated experiments ($T = f^{-1} = 0.1$ s) both thermal decays appear instantaneously. Thus, η_{NR} is expected to be in a four-level laser system:

$$\eta_{\text{NR}}(\hbar\omega_{3,0}) = \eta_{3,2}(E_{3,2}/E_{3,0}) + \left(\frac{W_{\text{NR}}}{W_{\text{R}} + W_{\text{NR}}} \right) (E_{2,1}/E_{3,0}) + \eta_{1,0}(E_{1,0}/E_{3,0}) + \eta_s(E_3), \quad (1)$$

where E_0 indicates the ground state and $E_{3,0}$ is the absorbed photon energy: $\hbar\omega_{3,0} = E_3 - E_0$, W_{R} (W_{NR}) is the radiative (nonradiative) emission probability of the upper laser level, and $\eta_{j+1,j}$ is the nonradiative energy-conversion efficiency between levels $(j + 1)$ and (j) . The term $\eta_s(E_3)$ due to the presence of non-radiative surface layers (NRSLS) [3] has been added in Eq. (1) with no *a priori* knowledge of its effect, magnitude, or spectral behavior.

Regarding the spectral minima in the $\eta_{\text{NR}}(\hbar\omega)$ curves as indicative of the non-radiative quantum efficiency of the metastable laser level,

$$\eta_{NR}^{(\omega)} = W_{NR} / (W_R + W_{NR}) , \quad (2)$$

an upper limit in that quantity may be calculated without further knowledge of $\eta_r(\hbar\omega)$:

$$\eta_{NR}[(\hbar\omega)_{\min}] \geq \eta_{NR}^{(\omega)} \left(\frac{E_{2,1}}{E_{2,0}} \right) . \quad (3)$$

For $Ti^{3+}: Al_2O_3$, we may take the peak of the fluorescence spectrum at 760 nm (Ref. 6) as $\bar{E}_{2,1}$ and $E_{2,0} \sim (\hbar\omega)_{\min}$. This yields, from Fig. 3 for our various samples

$$\begin{aligned} \eta_{NR}^{(\omega)}(Ti^{3+}:Al_2O_3)_{\text{thin}; FOM=40} &\leq 13.80005\% , \\ \eta_{NR}^{(\omega)}(Ti^{3+}:Al_2O_3)_{\text{thin}; FOM=800} &\leq 12.70005\% , \\ \eta_{NR}^{(\omega)}(Ti^{3+}:Al_2O_3)_{\text{thick}; FOM=40} &\leq 1.90005\% , \\ \eta_{NR}^{(\omega)}(Ti^{3+}:Al_2O_3)_{\text{thick}; FOM=800} &\leq 2.40005\% . \end{aligned} \quad (4)$$

Detailed theoretical models of the $Ti^{3+}: Al_2O_3$ system are currently under investigation, [7,8] extended to incorporate $\eta_{NR}(\hbar\omega)$ and $\eta_{NR}^{(\omega)}$ information for better quantification of the latter quantity and for our understanding of the role of NRSLS.

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