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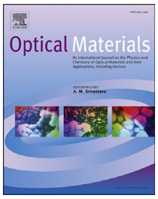

Ti:sapphire – A theoretical assessment for its spectroscopy

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ABSTRACT

This article tries to theoretically compute the stimulated emission cross-sections when we know the oscillator strength of a broad material class (dielectric crystals hosting metal-transition impurity atoms). We apply the present approach to Ti:sapphire and check it by computing some emission cross-section curves for both π and σ polarizations. We also set a relationship between oscillator strength and radiative lifetime. Such an approach will allow future parametric studies for Ti:sapphire spectroscopic properties.

1. Introduction

Progress in high power solid state lasers such as those of the PetaWatt class require good knowledge and understanding of the spectroscopic properties of very large Ti:sapphire single crystals. We need to know these photo-physical properties for samples which may have large dimensions: tens of centimeters. Here we present a method for estimating an order of magnitude of the stimulated emission cross-sections of Ti:sapphire, which is an essential parameter to predict laser behavior in computer simulations.

This material has been extensively studied, both from theoretical and experimental points of view ([1–3]). Ti^{3+} doped compounds including Ti:sapphire have been successfully treated either from molecular orbital theory or ligand field theory. Within these two contexts, we have a good knowledge of the 3d radial expectation values of powers $\langle r^3 \rangle$, but we want to emphasize that we did not need to use them in this work. P. Albers [3] made calculations assuming the relaxation from the Laporte's rule for that material due to the absence of a center of symmetry. This absence is then responsible for residual dipole matrix elements. A real vibronic contribution is also involved. The relaxation from the Laporte's rule indicates a lowering of symmetry from O_h to C_{3v}. If we assumed an O_h symmetry, then the odd components of the crystal field would identically vanish and the well known d-p mixing would not occur. So we stress that the true point symmetry in Ti:sapphire is C_{3v} (or C_3). A d-p mixing (all orbitals belong to the titanium ion) is then at work and it causes these dipole matrix elements. Moreover we know that in an opposite parity configuration mixing the wavefunction radial part cannot be treated as 3d radial expectation values. We claim that we do not use these radial part values neither the very crude point charge model. We have released ourselves from the latter model given in Ref. [4] and we have used no formula for the moment constants. We do indeed not use at all any formulation of the crystal field and we merely refer to the one-electron electric dipole moment table without formula for these moments. The distribution of moments in Table 1 only obeys the qualitative geometry of the corundum. The evocation of the mixture d-p is exploited to produce the residual electric moments. Other points of view or theories could be evoked to explain the appearance of such residual electric moments.

We follow the logical way of measuring the light absorption which can give us information about the values of the dipole strengths. A simple Huang-Rhys model [5,6] is used to take into account the lattice influence on the titanium ion. This model implements the contribution from overlap integral and gives us a simple and analytical spectral shape for spontaneous emission spectra.

We will present all the assumptions of our model and hope to relax some in future papers. We aim at understanding Ti:sapphire spectroscopy to better design lasers. As key novelties, we bring some new computed values for the stimulated emission cross-sections of Ti:sapphire. We also show a very important relationship between the oscillator strengths and the radiative lifetimes. This relationship is indeed a novelty because it takes into account

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Table 1
Electric dipole moments for Ti:sapphire (ref [4]).

	M_x	M_y	M_z
e_xt_x	A	$-2\sqrt{2}D$	C
e_yt_y	$-A$	$2\sqrt{2}D$	C
e_xt_y	$-2\sqrt{2}D$	$-A$	$-3D$
e_yt_x	$-2\sqrt{2}D$	$-A$	$3D$
e_xt_z	B	$-D$	0
e_yt_z	D	B	0

the level degeneracy of our material. We thus made the fundamental assumption of a single set of Huang-Rhys parameters for all possible emission transitions. The authors claim its novelty and confirm that they have not seen it in other scientific articles. The very useful method which we used is termed in French: ”la méthode de la résolvante”. This method can be consulted in Ref. [7].

2. Main assumptions

2.1. The Born-Oppenheimer scheme

According to the arguments given by I.B. Bersuker [8] and V.Z. Polinger [9], the separation between the electronic and nuclear variables of our system can be rigorously set when the following condition is fulfilled:

$$\hbar\omega_\Gamma(m) \ll |E_k - E_m| \text{ for all } k \neq m \text{ and any } \Gamma \tag{1}$$

Γ may be an irreducible representation of the symmetry site, E_k or E_m denote the energies of the states k and m. $\omega_\Gamma(m)$ stands for the vibration quantum relative to the active mode of the Γ representation. When this condition is checked, it allows to use the Born-Oppenheimer scheme where we first solve the electronic problem and use its solutions to study the vibrational motions of the nuclei. For our system, the only true assumption is to regard the radiative transitions among these electronic multiplets as adiabatic. Such an assumption does remain an approximation. This analysis follows the line of argumentation given by Yu.E. Perlin et al. [10].

2.2. The spectral shape on radiative transitions

Another fundamental assumption involves the superposition of simple bands with different Stokes shifts and intensities (depending on the dipole strengths). This is consistent with what is said in Ref. [10]. We are interested in spontaneous and stimulated emissions. We observe that the spectral shape of these emissions is Gaussian at high temperatures and does not show a double-band internal structure as the one seen for absorption spectra. So our first innovation is to only regard one set of Huang-Rhys parameters (one S factor and the single phonon frequency ω_l) although we should normally use different sets for each electric dipole moment. This will allow us to factor the spectral shape for the spontaneous emission process. We do not use the calculated spectral shape of a parity-forbidden transition because we do not observe a valley (zero value) at the wavelength corresponding to the most probable Stokes shift (given by the Franck-Condon principle). For our theory, the spectral shape is due to residual but allowed dipoles. This is described by a simple Huang-Rhys model.

2.3. The complete lifting of degeneracy

According to crystal field theory, the electronic levels of the titanium ion undergo a progressive lifting of degeneracy when we regard lower and lower symmetries. We have the scheme:

$$O_h \supset C_{3v} \supset C_3 \tag{2}$$

The highest symmetry is cubic or octahedral O_h (it is not the true point symmetry in Ti-sapphire; we regard it as an approximation). For this symmetry, we have a doublet e_g and a triplet t_{2g}. As stated by McClure [4], the absence of a center of symmetry in corundum means that the $d \rightarrow d$ transition can occur because odd-power terms may mix the even d functions with odd functions. The latter are titanium 4p orbitals. This absence then indicates that we are considering the lowering of symmetries form $O_h \rightarrow C_{3v}$. When symmetry is further lowered, the symmetry group C_3, which is a cyclic group [4], is gained. The latter is a commutative group. As we know that all irreducible representations associated with a commutative symmetry group have dimension one (they are not degenerate), we can conclude that all sates in such a crystal field (C_3 symmetry) are non degenerate. We are here concerned exclusively with one electron transitions of the type $e \rightarrow t$. The notations e or t refer back to the electronic states e_g and t_{2g} before the splitting of the degenerate states. For the symmetry C_{3v} the dipole matrix elements are expressed thanks to three moment constants A, B and C. When we further lower the symmetry, we have to introduce another constant D. D is lower than A,B and C and the former will be neglected. We want to stress that the notations e and t for the states were defined by C.J. Ballhausen [11]. The dipole matrix elements are expressed between states (e_x, e_y) and (t_x, t_y, t_z). As a result we are allowed to define radiative lifetimes of the excited energy level e by using the moment Table 1. (e_x, e_y) and (t_x, t_y, t_z) are not states of the symmetry O_h. They are states associated with energy levels of the symmetry C_{3v}.

2.4. A dilute doping concentration

Our material is Ti:Al$_2$O$_3$. The samples may have typical Ti concentrations of about 3.3×10^{19} cm^{-3} as stated in Ref. [1]. Experimental spectroscopic values may have been obtained with such concentrations.

We know that the electron-phonon coupling factors (as provided for example by a simple Huang-Rhys model) may vary with doping concentrations [12]. So our model may be inaccurate if doping concentrations vary over a wide range or have large spatial variations.

Furthermore, we assume that the doping concentrations are small (they may be smaller than 3.3×10^{19} cm^{-3}) so that we may neglect the interaction between ion impurities. The spectroscopic properties are then independent of these concentrations. In the formulas for oscillator strengths or stimulated emission cross-sections, there is no impurity concentration factor. We recognize that a weak concentration of Ti is not the best for laser applications for which self-quenching may play a role. We are aware of these serious limitations of our model. Further work will include dopant concentration, which may be done by varying the Huang-Rhys parameters accordingly.

3. Theory and experimental test

3.1. A process chain for the computation of quantitative spectroscopic properties

The true site of Ti ion in corundum is trigonal. There is no triple degeneracy for Ti:sapphire. Nevertheless we can track back the eigenstates to those found for the octahedral symmetry.

The usual and the easiest way to measure the dipole strengths is conducting a light absorption experiment. The latter will measure the oscillator strength and will finally give us dipole strengths.

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