Journal of Alloys and Compounds 275–277 (1998) 174–176

Energy level and oscillator strength calculations for Er^{3+}:Y_2O_3: A molecular dynamics based study

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Abstract

A molecular dynamics (MD) based approach is being developed to calculate energies and oscillator strengths for RE ions in various solid/liquid/amorphous inorganic compounds. In this connection, the complete 364×364 energy matrix for the $Er^{3+}(4f^{11})$ electrons has been diagonalized for different MD-generated environments. The importance of MD is emphasized. Configuration interaction (CI) effects are included in constructing the energy matrix, since these have a significant influence on the derived absorption spectrum. The A_{tp} parameters have been calculated by direct summation over 100 multipole-expanded environments generated with MD. The various polarizabilities and shielding parameters used have been calculated by ab initio methods. The derived energies and eigenvectors have been used to compute the oscillator strengths and the corresponding spectra. Both electric-dipole and inhomogeneous dielectric mechanisms have been considered in the oscillator strength calculation. The calculated Stark splittings and oscillator strengths for the Stark–Stark level transitions agree well with experiment for Er^{3+}:Y_2O_3. The best agreement is obtained when consistent multipole contributions are included in the converged calculated crystal field. The method described above is important in predicting a priori laser related properties (radiative lifetimes, etc.) for potential host materials. © 1998 Elsevier Science S.A.

Keywords: Er^{3+}:Y_2O_3; Molecular dynamics; Oscillator strength

1. Introduction

Rare-earth doped Y_2O_3 has received considerable attention over the years since the oxide lattice is a first-rate laser host material. The Stark energy level, absorption and emission probabilities between *J*-manifolds and radiative lifetime studies can be found in the literature [1–5]. It is well known that the cubic Y_2O_3 lattice has two different sites for Er^{3+} ion substitution. The unit cell has three sites with point-group symmetry C_2 and one with point-group symmetry C_{3i}. Since the C_{3i} site is an inversion centre, the electric-dipole transitions are not allowed for Er^{3+} ions occupying these sites. As a consequence, the experimental data (e.g., crystal-field splittings and intensities) for rare-earth ions at these sites is sparse, since the peaks are generally attributed to the ions on the C_2 sites. The assumption that electric-dipole transitions are not allowed is only approximately true; the thermal fluctuations (i.e. various environments) of the Y_2O_3 lattice destroy the perfect C_{3i} point-group symmetry locally, thus allowing the electric-dipole transitions.

In this and earlier work by the authors [6–11] (where extensive theoretical detail is given) a molecular dynamics (MD) simulation has been used to generate an ensemble of physically acceptable rare-earth ion environments. It will be emphasized that the deviations from the perfect crystalline structure cannot be ignored, even at low temperatures, when calculating polarized Stark–Stark level oscillator strengths. This is because the oscillator strengths have a quadratic crystal field (CF) dependence ($|A_{tp}|^2$) and therefore do not average out around an inversion centre. This can be compared to the situation for energies, which have a linear CF dependence (A_{tp}), so that these effects average out and are thus less important. Our MD approach has allowed us to study the difference between C_2 and C_{3i} sites in calculating oscillator strengths and polarized absorption spectra.

2. The theory and the computational procedure

The energies and eigenvectors needed for the construction of a absorption/emission spectrum are obtained by diagonalizing the energy matrix. This matrix is most easily constructed by calculating the matrix elements in the

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PII: S0925-8388(98)00297-7

γSLJM representation using the standard Hamiltonian $H = H_{\mathrm{EL}} + H_{\mathrm{SO}} + H_{\mathrm{CI}} + H_{\mathrm{CF}}$

$$\langle \gamma SLJM|H|\gamma' S' L' J' M'\rangle \qquad (1)$$

The different terms in the Hamiltonian (H) represent the Coulomb, spin–orbit, linear and non-linear configuration (second-order) and crystal field interactions, respectively. It should be noted that the complete 364×364 matrix has been computed and diagonalized directly, implying that both intermediate-coupling and JJ-mixing effects have been accounted for. Details as to the different matrix elements computed can be found in Refs. [7,8], and the values of the free-ion parameters used are given in Table 1.

The MD technique solves Newton's equations of motion to give the positions and velocities for all ions in the simulation box at each time step. A standard ion-pair MD potential of the Born–Mayer–Huggins form (2) has been used in the MD simulation to generate the force field:

$$V_i = \sum_{i\neq j} q_i q_j / r_{ij} + A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 \qquad (2)$$

It is important not to confuse Eq. (2), which is the molecular dynamics potential, with the crystal field potential that is used in the construction of the energy matrix. The crystal field potential has been treated with standard methods (see Eqs. (5)–(13) of Ref. [7], and Ref. [12]). The MD potential parameters, A_{ij}, ρ_{ij} and C_{ij}, are fitted to reproduce the crystal structure; these are also listed in Table 1. The simulation box for Er^{3+}:$\mathrm{Y_2O_3}$ of 3×3×3 unit cells contains 2160 atoms, including two Er^{3+} ions (corresponding to: 6.21×10^{19} ions cm^{-3}; 0.23% substitution of the Y-sites; and 0.34 wt% Er^{3+}:$\mathrm{Y_2O_3}$). The simulation was initialised and equilibrated for 4000 time steps with $\Delta t = 1.0$ fs and $T = 77$ K.

The lattice summations (necessary for evaluating the CF parameters A_{tp} used in H_{CF}) have been made over all point charges within 70 Å, and over all consistent dipole and quadrupole moments within 8 Å of the Er^{3+} ion. Many authors have proposed the use of more ''sophisticated'' CF models [12–14] to replace the simple electrostatic model. However, our MD treatment shows very large fluctuations (sometimes even up to ±200%) to occur in the CF parameters. For this reason it is important to fully explore the electrostatic model before invoking more ''sophisticated'' models. The polarized oscillator strengths are given by

$$P_q(i,f) = \frac{1}{2}\chi \frac{8\pi^2 m\nu}{h} |\langle i|D_q^{(1)} + W^{\mathrm{IDM}}|f\rangle|^2 \frac{\mathrm{e}^{-E_i/k_{\mathrm{B}}T}}{\sum \mathrm{e}^{-E_i/k_{\mathrm{B}}T}} \qquad (3)$$

where $\langle i|$ and $|f\rangle$ are the initial and final states for the system, and $D_q^{(1)}$ and W^{IDM} are the electric dipole operator and inhomogeneous dielectric operator, respectively [7,15–17]. The ground-state levels are assumed to have a Boltzmann population. If the material is cubic (optically isotropic), the oscillator strength is given by

$$P(i,f) = \tfrac{1}{3} \sum_{q=-1,0,1} P_q(i,f) \qquad (4)$$

i.e. the polarization is summed out.

3. Results and conclusions

Fig. 1 shows the calculated absorption spectrum for Er^{3+}:$\mathrm{Y_2O_3}$. Since Er^{3+}:$\mathrm{Y_2O_3}$ is cubic, Eq. (4) has been used to calculate the oscillator strengths. The only experimental absorption spectrum available [4] is plotted in Fig. 1d,e. Plots (b) and (c) are the corresponding calculated transitions with the $\mathrm{C_2}$ and $\mathrm{C_{3i}}$ contributions added and appropriately weighted. The qualitative agreement between experiment and theory is clear as regards the overall shape of the transition manifolds. As a consequence of the uncertainties in the free-ion parameters, the multiplets are shifted slightly to longer wavelengths. In Fig. 2, the contributions from Er^{3+} ions in a $\mathrm{C_2}$ and a $\mathrm{C_{3i}}$ symmetry

Table 1
The free-ion parameters [1,18] and the molecular dynamics potential parameters used in the calculations

Free-ion parameters		Molecular dynamics parameters				
Parameter	Er^{3+}:$\mathrm{Y_2O_3}$ (cm^{-1})	i	j	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å^6)
F^2	96658.8	O	O	22764.3	0.149	27.8
F^4	70831.1	O	Y	1450.0	0.355	0.0
F^6	52563.4	O	Er	2000.0	0.36	0.0
ζ	2366.0	Y	Y	0.0		0.0
α	27.7	Y	Er	0.0		0.0
β	−811.0	Er	Er	0.0		0.0
γ	1018.0					
T^2	662.0					
T^3	58.0					
T^4	51.0					
T^6	−281.0					
T^7	515.0					
T^8	515.0					
τ	0.87					

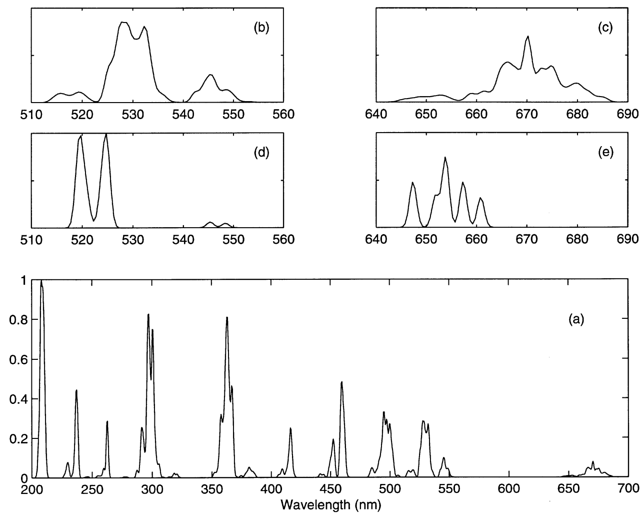

Fig. 1. (a) The calculated absorption spectrum for Er^{3+}:Y_2O_3 in arbitrary units. The calculated spectra (a,b,c) are plotted with the C_2 and C_{3i} contributions summed and appropriately weighted. The experimental spectra are plotted in (d) and (e).

site are plotted above and below the line, respectively. Fig. 2 clearly illustrates the sometimes critical importance of taking the deviations from the perfect crystalline structure of the ions into account. The contribution from Er^{3+} ions in C_{3i} symmetry sites is not negligible, especially around 300 and 380 nm. To compensate for the small number of simulated environments used, each transition has been assigned a Gaussian distribution. The band widths in the derived spectrum are slightly too large (see, for example, Fig. 1c,e), which indicates that the ions are ''too mobile'' in the MD simulation.[1] A re-examination of the MD potential parameters presented in Table 1 might therefore be appropriate.

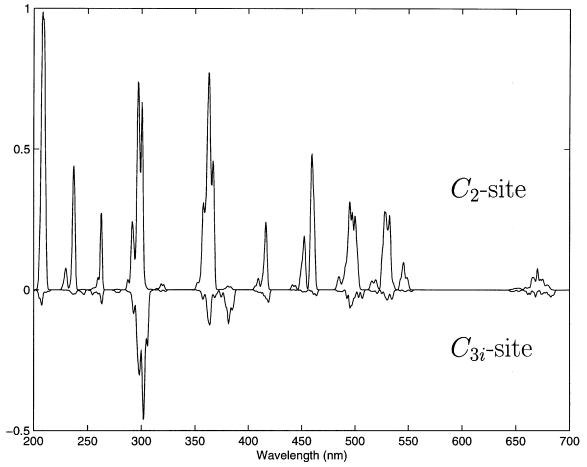

Fig. 2. The calculated absorption spectrum for Er^{3+}:Y_2O_3 in which the contributions from Er^{3+} ions in a C_2 symmetry site are plotted above the line, and those from Er^{3+} ions in a C_{3i} symmetry site below the line.

We conclude that an MD (or Monte Carlo) approach can sometimes be crucial to a successful calculation of Stark–Stark oscillator strengths and the corresponding absorption/emission spectra. The use of an electrostatic CF model within an MD approach should be examined fully before invoking the more ''sophisticated'' (and sometimes more realistic) crystal field models.

Acknowledgements

This work was supported by grants from The Swedish Natural Science Research Council and The U.S. Office of Naval Research.

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[1] We have performed an additional simulation at $T=35$ K. This simulation displays narrower peaks and also that the contributions from C_{3i} sites are important for the transitions around 380 and 300 nm (even at $T=35$ K).