Crystal field parameter calculations for doped Pr^{3+} ion in Y_2SiO_5 crystal

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Ab initio calculation of $^1D_2$ term split of a Pr^{3+} ion in Y_2SiO_5 crystal for two non-equivalent optical centers is carried out. The calculated splitting values agree satisfactorily with experimental data and allow to ascribe uniquely the spectral lines belonging to different optical centers.

Проведен *ab initio* расчет расщепления терма $^1D_2$ иона Pr^{3+} в кристалле Y_2SiO_5 для двух неэквивалентных оптических центров. Рассчитанные величины расщепления удовлетворительно согласуются с экспериментальными данными и позволяют однозначно соотнести спектральные линии, принадлежащие различным оптическим центрам.

Yttrium oxyorthosilicate Y_2SiO_5 crystals doped with rare-earth atoms are widely known due to the use thereof in cathodoluminescence, laser, and scintillation technique. Today, these crystals are considered to be potential materials for optical memory cells [1], luminescent markers of biological objects [2], etc.

A distinctive feature of crystals is that the doping rare-earth atoms may be localized in different non-equivalent positions that are characterized by low-symmetry surroundings. During the crystal growing, the allocation of the impurity element in non-equivalent positions occurs at different probabilities. To understand why one position for impurity ion is more preferable than the other, it is necessary to know which type of light spectrum belongs to the definite position. It is impossible without calculation of term split in the specific crystal position.

The low symmetry of C_1 position that is occupied by rare-earth ions in Y_2SiO_5 crystals makes impossible to use the method of crystalline field parameter adjustment on the observed splitting of terms obtained from absorption and luminescence spectra. Therefore, it is necessary to evaluate that

splitting from the first principles and its knowledge can be used at evaluation of other physical properties. Although the problem is under study rather long, it is not always possible to attain an acceptable precision of term split calculations for quantitative comparison to real results [3]. However, as it will be shown below, the calculation of energy parameters of the Pr^{3+} doping ion crystalline field allows to interpret unambiguously the apparent optical centers to a specific crystallographic position.

The electrostatic model in point approach was used to calculate the energy parameters of a crystalline field for the doping Pr^{3+} ion in Y_2SiO_5 crystal matrix. According to this model, the parameters of a crystalline field are defined in the following way:

$$B_{kq} = \sum_j - \sqrt{\frac{4\pi}{2k+1}} \ e^2 <r^k> \frac{C_j}{R_j^{k+1}} Y^*(\alpha_j, \beta_j),$$

where B_{kq} are the crystalline field parameters; $\langle r^k \rangle$, average value of electron radius in $4f$ shell; C_j, value of point charges that surround the doping ion; R_j, α_j, β_j, spherical coordinates of the surrounding charges.
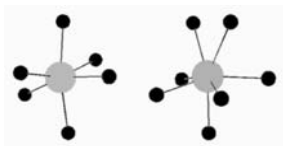
Fig. 1. Two non-equivalent Y^{3+} positions in Y_2SiO_5 crystal. The first one is yttrium ion in 6 oxygen environment; second, in 7 oxygen environment.

The shielding effect was taken into account in the calculations by multiplying $\langle r^k \rangle$ by expression $(1 - \sigma_k)$ [4].

The energy split of $^1D_2$ term of the Pr^{3+} ion was evaluated by diagonalization of the energy matrix:

$$<4f^2 LSJM_j \left| \sum_{kji} B_{kq} Y_{kq}(\theta_i, \varphi_i) \right| 4f^2 LSJM_j'>,$$

where θ_i, φ_i are spherical coordinates of i-th electron in the Pr^{3+} ion. It is possible to reduce the energy matrix using the technique of irreducible tensor operators [5] to the following view:

$$\sum_{k,q} (-1)^{M_j+1} 2B_{kq}(2J+1)(2L+1) \times$$

$$\times \begin{Bmatrix} L & J & S \\ J & L & k \end{Bmatrix} \begin{Bmatrix} l & L & l \\ L & l & k \end{Bmatrix} \begin{pmatrix} J & k & J \\ -M_j & q & M'j \end{pmatrix} (l \| Y_k \| l),$$

where $(l \| Y_k \| l)$ are the adduced matrix element of surface function for $4f$ shell; { }, ( ) the $6j$ and $3j$ Raka symbols.

The Y_2SiO_5 crystals belong to the monoclinic syngony of the $B2/b$ space group. The unit cell contains 64 atoms and has the following sizes: $a = 14.40$ Å, $b = 6.723$ Å, $c = 10.410$ Å, $\beta = 122.179°$ [6]. The positions of all atoms of a crystalline lattice were defined by application of the symme-

Table 1. Position of atoms in Y_2SiO_5 crystal evaluated in basic transmission parts

	x/a	y/b	z/c
Y1	0.35846	0.12288	0.16508
Y2	0.46308	−0.24491	0.03476
Si	0.31881	0.59041	0.19304
O1	0.29603	0.14508	0.3287
O2	0.48271	0.09589	0.10350
O3	0.59031	−0.49764	0.14106
O4	0.29905	0.43142	0.06204
O5	0.38165	−0.21568	0.17891

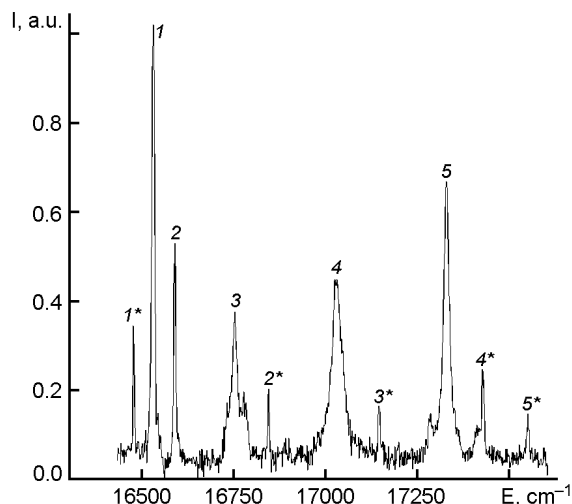
Fig. 2. A fragment of Y_2SiO_5:Pr^{3+} crystal absorption spectrum in transition $^3H_4 \rightarrow {}^1D_2$ at $T = 4.2$ К. Lines belonging to the first optic center are denoted by numbers and those belonging to the second one, by numbers with asterisks.

try space group element to basic atoms submitted in Table 1. The doping ions Pr^{3+} can replace isomorphically two nonequivalent positions Y^{3+} which are characterized by a various oxygen surrounding (Fig. 1). In the first position, the doping ion has 6 ions of oxygen in the nearest environment, while having 7 in the second one. The crystal field energy parameters of Pr^{3+} ion were obtained using the crystallographic data for all atomic positions in the crystal and $\langle r^k \rangle$ and σ_k values [7, 8] submitted in Table 2. The calculated crystalline field energy parameters for two non-equivalent positions are summarized in Table 3.

The detailed research of the doped Pr^{3+} ion in Y_2SiO_5 crystal has allowed to establish unambiguously the presence of two optical centers and to compare the observed lines in optical spectra to one of the centers [9]. Fig. 2 shows the absorption spectrum of a Y_2SiO_5:Pr^{3+} crystal at helium temperatures in the $^3H_4 \rightarrow {}^1D_2$ transition region. The same figure shows the lines of transi-

Table 2. Average radius values and shielding parameters values of praseodymium ion for $4f$ atom shell

k	2	4
$\langle r^k \rangle$ (at.un.)	1.086	2.82
σ^k	0.672	0.091

Table 3. Crystal field parameters for Pr^{3+} in Y_2SiO_5 for two non-equivalent cation sites.

	I center	II center
B_{20}	274.54	−104.207
B_{21}	−79−453i	315+63i
B_{22}	344+345i	−363+275i
B_{40}	33	−623
B_{41}	−1072+307i	−425+118i
B_{42}	703−113i	247+91i
B_{43}	550+464i	358−811i
B_{44}	925−55i	133−265i

Table 4. Calculated and experimentally observable splitting values of $^{1}D_2$ term of Pr^{3+} ion

I center (cm^{-1})		II center (cm^{-1})	
calculation	experiment	calculation	experiment
0	0	0	0
89	62	327	371
245	223	564	670
526	498	866	952
818	798	988	1077

tions concerning each center. Table 4 presents the results of $^{1}D_2$ term split calculations of and the experimentally observed splitting. The comparison of the results obtained shows that the calculation provides a rather satisfactory coincidence with the experimentally observed splitting.

Thus, the calculation of $^{1}D_2$ term split of the doping Pr^{3+} ion in Y_2SiO_5 crystal in electrostatic model of point approach is well conformed to the experimental results and allows to ascribe definitely the observed luminescence centers to specific crystallographic positions. We can say for sure basing on the data that during the yttrium oxyorthosilicate crystal growth, the doping Pr^{3+} ion occupies mainly the first non-equivalent position.

References

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Розрахунок параметрів кристалічного поля для домішкового іона Pr^{3+} у кристалі Y_2SiO_5

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Проведено *ab initio* розрахунок розщеплення $^{1}D_2$ терма іона Pr^{3+} у кристалі Y_2SiO_5 для двох нееквівалентних оптичних центрів. Розраховані величини розщеплення задовільно узгоджуються з експериментальними даними та дозволяють однозначно співвіднести спектральні лінії, що належать різним оптичним центрам.