Optical spectroscopy of random deformations in elastically-anisotropic crystals containing rare-earth ions

B.Z. Malkin[1,*], E.I. Baibekov[1], N.M. Abishev[1], D.S. Pytalev[2], M.N. Popova[2], and M. Bettinelli[3]

[1]Kazan Federal University, 420008 Kazan, Russia
[2]Institute for Spectroscopy RAS, 108840 Moscow, Troitsk, Russia
[3]Dipartimento di Biotecnologie, University of Verona and INSTM, 37134 Verona, Italy

Abstract. We present the results of studies of spectral effects in the optical high-resolution (0.01 cm-1) spectra of rare-earth ions in crystals caused by random deformations of a crystal lattice. Low-temperature polarized transmission spectra in a broad spectral range (5000–15000 cm^{-1}) were taken for tetragonal single crystals ABO4 (A=Y, Lu; B=V, P) containing impurity Tm^{3+} ions with concentrations 0.2 and 1.0 at.%. A specific fine structure of singlet-doublet transitions in the Tm3+ ions was observed. We demonstrate a possibility to estimate a concentration of intrinsic lattice defects from the analysis of the measurement data, by making use of an analytical expression derived in the present work for the distribution function of random lattice strains induced by point defects in the elastically-anisotropic continuum.

Modulation of crystal fields by random lattice deformations brings inhomogeneous broadening of spectral lines. Random deformations are also responsible for a specific fine structure of transitions which involve degenerate crystal-field sublevels of rare-earth ions in the crystal fields of cubic, tetragonal, or trigonal symmetry [1-3].

In the present work, we measured polarized high-resolution (0.01 cm^{-1}) transmission spectra of RVO_4 and RPO_4 (R=Y, Lu) crystals with the zircon structure containing impurity Tm^{3+} ions (0.2 and 1 at.%) which substitute for the R^{3+} ions at sites with the local tetragonal D_{2d} symmetry. At temperatures below 15 K, we observed a doublet structure of the spectral lines corresponding to transitions between the singlet (doublet) and doublet (singlet) crystal-field sublevels of the ground multiplet $^3H_6$ and excited multiplets $^3F_4$, $^3H_5$ and $^3H_4$, respectively, of the Tm^{3+} ions. These lines have a specific shape (see Fig. 1) with a narrow (as compared with a full line width at half maximum) dip at the center and the splittings between the maxima from 0.04 up to 0.16 cm^{-1} for different lines, increasing with the concentration of the tulium ions and markedly exceeding hyperfine splittings of the doublets.

Calculations of crystal-field energies of the Tm^{3+} ions in the deformed crystal lattice were carried out using the Hamiltonian that involved energies of 4f-electrons in the free

* Corresponding author: boris.malkin@kpfu.ru

ion, hyperfine interactions, crystal-field and electron-deformation interactions. Parameters of the electron-deformation interaction were calculated in the framework of the exchange-charge model and corrected by the analysis of the piezo-spectroscopic measurements [4].

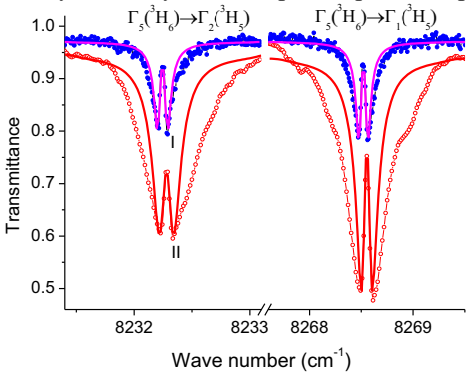

Fig. 1. Fragments of the measured transmission spectra of YVO_4 single crystals doped with Tm^{3+} ions (0.2 at.% (I) and 1.0 at.% (II)) at T=4 K (symbols). Solid lines represent results of calculations.

The envelopes of the spectral lines were obtained by averaging transition intensities calculated for fixed values of the strain tensor components with the distribution function of strains induced by point defects in the elastically-anisotropic continuum. The derived analytic expression for the distribution function presents the generalized Lorentz distribution in the six-fold space of the strain tensor components e_α $(\alpha = 1:6)$: $g(\boldsymbol{e}) = (15\gamma/8\pi^3)\det|\nu_{\alpha\beta}|\sum_{\alpha,\beta=1}^{6}(\nu_{\alpha\beta}e_\alpha e_\beta + \gamma^2)^{-7/2}$. Here, $\nu_{\alpha\beta}$ are coefficients in the positively determined quadratic form constructed from the strain tensor components. Values of these coefficients were found using Green's functions of the elastic theory equations [5] computed for the sets of elastic constants of the studied crystals. Examples of the calculated envelopes of the spectral lines are shown in Fig. 1. As follows from a comparison of the computed and measured spectra, interactions between the impurity ions contribute markedly into the line widths even in crystals with relatively small concentrations (of about 1%) of impurity ions.

When both concentrations of the intrinsic point lattice defects (C_i) and of the impurity ions (C_{Tm}) are small enough, the width γ of the distribution function is a linear function of C_i and C_{Tm}. Using the widths γ obtained from the analysis of the measured line shapes of different singlet-doublet transitions in crystals with concentrations of 0.2 and 1 at.% of the Tm^{3+} ions, we estimated concentrations of intrinsic lattice defects. Even in the crystals of high optical quality, the width of the random strains distribution, corresponding to the intrinsic defects, is not less than $(3 - 5)\,10^{-5}$. The results of the present work open a possibility to connect the observed spectral effects with the defect «strength» and may serve as a basis for the elaboration of the quantitative method of crystal quality control.

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