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JOURNAL OF RARE EARTHS

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JOURNAL OF RARE EARTHS, Vol. 32, No. 3, Mar. 2014, P. 230

High-resolution Fourier spectroscopy as a tool for studying quality of rare-earth-doped crystals

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Received 9 June 2013; revised 9 September 2013

Abstract: Three examples were considered of the use of high resolution Fourier-transform optical spectroscopy for studying quality of rare-earth-doped crystals. The first example was connected with defects present in crystals grown by flux techniques. The second example dealt with detection of stresses and deformations in rare-earth-containing crystals, by registering splitting of spectral lines. The third example showed that a very small amount (at the level of ppm) of different RE ions present in a crystal could be determined using high-resolution spectroscopy. This work was carried out by the author's group in collaboration with several institutions in Russia and abroad.

Keywords: Fourier-transform optical spectroscopy; high resolution; absorption spectra; rare earths

Optical spectra of rare-earth (RE) ions in crystals are, mainly, due to parity forbidden f-f transitions that become allowed due to odd components of the crystal field. The 4f-shell is well shielded from a crystalline environment by the filled 5s and 5p shells, and the crystal field acts as a weak perturbation to the energy levels of a free RE ion. Due to slightly different environments experienced by different RE ions in a real crystal, spectral lines from an ensemble of RE ions broaden. However, this inhomogeneous broadening is small in many cases (0.001–0.1 cm^{-1}, see, e.g., Refs. [1,2]), which delivers a possibility to study the presence of point defects, strains, other (unwanted) RE ions in a sample. The f-f spectra of RE ions extend from the far infrared to ultraviolet range, the most intense optical transitions allowed for a free ion lie in the infrared range. Registering such high-resolution spectra with a Fourier spectrometer rather than with a grating one gives a tremendous gain in sensitivity, resolution, and precision of the wavenumber scale[3].

Three examples of the use of high-resolution Fourier spectroscopy for determing the quality of crystals are considered. The first example is connected with defects present in multifunctional nonlinear laser crystals from the family of rare-earth borates with the structure of the natural mineral huntite. The method can be used, in particular, for a rapid detection of a molybdenum impurity that diminishes a transparency in the ultraviolet (UV) spectral region and for improvement of growth technique. The second example deals with detection of stresses and deformations in rare earth containing crystals, by registering splitting of spectral lines. This method may be useful for controlling the quality of crystals for, e.g., optical quantum memories. The third example shows that a very small amount (at the level of ppm) of different RE ions present in a crystal can be determined using high-resolution spectroscopy.

1 Experimental

Polarized optical absorption spectra in a spectral range of 1000–25000 cm^{-1} were measured using a high-resolution Fourier spectrometer Bruker IFS 125 HR. The method of Fourier spectroscopy is beyond comparison for taking broadband high-resolution spectra with a precise wavenumber scale. The resolution for the absorption measurements was up to 0.005 cm^{-1} and was chosen to reproduce correctly the narrowest details in the spectra. The spectra were registered in the α ($k \| c$, $E, H \perp c$), σ ($k \perp c$, $E \perp c$), and π ($k \perp c$, $E \| c$) polarizations. For low-temperature experiments, we used either a closed-cycle Cryomech ST403 cryostat or a helium-vapor cryostat.

2 Aluminum borates $RAl_3(BO_3)_4$

Aluminum borate crystals, especially $YAl_3(BO_3)_4$ (YAB), are important nonlinear optical materials with a wide band gap[4–6]. Doped with the Nd^{3+} or Yb^{3+} ions, they are efficiently used in self-frequency doubling and self-frequency summing lasers[7–12]. YAB crystals codoped with Yb^{3+} and Tm^{3+} are promising for up-conversion lasers[13,14]. Undoped YAB crystals are considered for the fourth harmonic generation of the Nd:YAG laser radiation.

Foundation item: Project supported in part by the Russian Foundation for Basic Research (13-02-01091)

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DOI: 10.1016/S1002-0721(14)60067-3

Rare-earth aluminum borates melt incongruently, so the single crystals can be grown only by a flux method. The first aluminium borates were obtained by Ballman in 1962 using the K_2SO_4-$3MoO_3$ and PbF_2-$3B_2O_3$ fluxes[15]. Later, Leonyuk et al. have suggested the $K_2Mo_3O_{10}$ flux[16] and succeeded in growing crystals up to 30 mm in size. Recently, various $RAl_3(BO_3)_4$ crystals of good optical quality and big size were obtained in the group of Bezmaternykh in the Kirenskii Institute of Physics, using a new $Bi_2Mo_3O_{12}$-Li_2MoO_4 flux[17]. Because of the flux growth method, it is very difficult to control growth defects, such as twinning, uncontrollable impurities from the solvent, etc. Such defects diminish an application potential of the considered crystals. For example, the molybdenum impurity restricts the use of YAB crystals in the UV spectral range[18]. Therefore, the problem of impurity control at different growth techniques is highly topical.

Recently, we have shown that the measurement of the fine structure of the zero-phonon $0(^2F_{7/2})\to0'(^2F_{5/2})$ absorption line of Yb^{3+} doped into a RAB crystal is a sensitive method for detecting uncontrollable impurities entering the crystal during the growth by a flux technique[19–21]. Using crystals specially grown with a flux containing excess molybdenum or bismuth components, we were able to identify satellites accompanying the 0–0 Yb^{3+} line in $R_{1-x}Yb_xAl_3(BO_3)_4$, (R=Y, Tm, Lu) crystals. Fig. 1 displays the high resolution spectra in the region near the 0–0 line of the Yb^{3+} ions which were doped in similar concentrations into YAB crystals grown independently in four different laboratories using different fluxes. The majority of the crystals were grown in the Kirensky Institute of Physics using a bismuth-lithium-molybdenum oxide solvent. The second group of YAB:Yb crystals was grown from flux based on potassium trimolybdate solvent. These crystals with different concentrations of Yb were grown in three different laboratories, namely in the University of Verona, in the Laboratory of Solid State Chemistry in Paris (LCMCP), and in the Moscow State University. The last group of YAB:Yb crystals was grown in LCMCP using LaB_3O_6 as the base for flux.

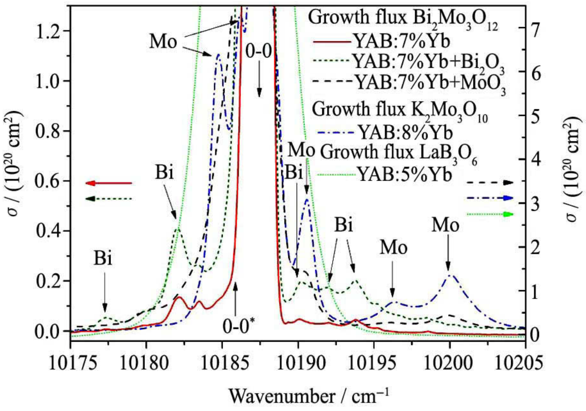

Fig. 1 Zero-phonon line $0(^2F_{7/2})\to0'(^2F_{5/2})$ of Yb^{3+} in YAB single crystals doped with Yb^{3+} in similar concentrations but grown by different solvents (T=3.6 K[21])

From the relative intensities of the satellite lines related to Mo impurities, it was determined that the concentration of molybdenum in YAB crystals grown with the $K_2Mo_3O_{10}$-based flux is more than 300-fold higher than in crystals grown with the $Bi_2Mo_3O_{12}$-based flux. As for the crystals grown from the flux based on LaB_3O_6, they obviously do not contain impurities like molybdenum and bismuth. The lanthanum is the only possible impurity in such crystals. It enters the crystal lattice substituting up to 20% of yttrium ions which results in ytterbium line broadening and shift[21].

In summary, our spectroscopic method can be used for a rapid analysis of the quality of crystals for UV lasers and for improvement of a flux solution technique used to grow laser crystals and crystals for the fourth harmonic generation of the Nd-YAG laser.

3 Detection of stress and deformations

Internal stress and deformations in a crystal may arise during the growth and annealing process, they also depend crucially on the mode of mounting a sample for measurements. In particular, a crystal on a cold finger of a cryostat is usually firmly pressed to the finger's surface or/and glued to it to ensure a good thermal contact. A strong stress that arises in this case can be detected via RE spectral line broadening and, especially, splitting. Fig. 2 shows as an example a drastic distortion of a spectral profile for a singlet-doublet optical transition in $LiYF_4$: Tm^{3+} when a thin sample is glued to a mount along its perimeter.

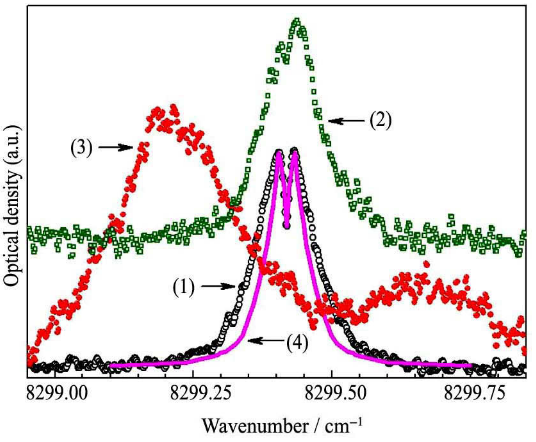

Fig. 2 Measured at T=4.3 K (1)–(3) and calculated (4) line shapes for the singlet-doublet transition $\Gamma_2(^3H_6)\to\Gamma_{34}(^3H_5)$ of Tm^{3+} in $LiYF_4$ (non-Kramers ion in S_4 symmetry position)

(1) $^7LiYF_4$:Ho (0.1 at.%), Tm (0.5 ppm) bulk sample (8.8 mm); (2) $^7Li_{0.93}{}^6Li_{0.07}YF_4$:Tm (0.1 at.%) sample (90 μm) placed free into a helium vapor in the helium-vapor cryostat; (3) the sample (2) but glued along its perimeter to a mount (The stress in the glued sample was estimated to be in the range of 8–28 MPa[22])