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ScienceDirect
Journal of Luminescence 127 (2007) 655–664
JOURNAL OF LUMINESCENCE
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# Side-hole to anti-hole conversion in time-resolved spectral hole burning of ruby: Long-lived spectral holes due to ground state level population storage

Hans Riesen[a,*], Brendan F. Hayward[a], Alex Szabo[b]

[a]School of Physical, Environmental and Mathematical Sciences, The University of New South Wales, ADFA, Northcott Drive, Canberra, ACT 2600, Australia
[b]Institute for Microstructural Sciences, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ont., Canada K1A 0R6

Received 20 December 2006; received in revised form 22 March 2007; accepted 30 March 2007
Available online 7 April 2007

**Abstract**

We report time-resolved transient spectral hole burning of Verneuil-grown 20 ppm and ca. 0.6 ppm ruby ($Al_2O_3$:$Cr^{3+}$) in zero field and low magnetic fields B$\|c$ at 4 K. The hole-burning spectroscopy of the 20 ppm sample implies relatively rapid cross relaxation in the $^4A_2$ ground state on the ~1 ms timescale both in zero field and in low magnetic fields, B$\|c$, up to 0.2 T. In the 0.6 ppm sample, side-hole to anti-hole conversion is observed both in zero field and in low magnetic fields. This conversion is caused by population storage in $^4A_2$ ground state levels. Spin-lattice relaxation, on the 200 ms timescale, is directly observed from the time dependence of the resonant hole and anti holes in B$\|c$, consistent with a very low cross-relaxation rate. However, in zero field cross relaxation in the $^4A_2$ ground state is still a significant relaxation mechanism for the 0.6 ppm sample resulting in hole decay in ~50 ms.


*Keywords:* Ruby; Transient hole burning; Time resolved; Cross relaxation; Spin-lattice relaxation; Zeeman effect; Anti holes; Side holes; Ground-state population storage

## 1. Introduction

Ruby is of great historical significance in the development of the spectroscopy of impurity ions in insulators. As early as 1867–1868 Becquerel [1] reported luminescence by the so-called *R*-lines ($^2E \rightarrow {}^4A_2$ transitions). In 1958 Tanabe and Sugano [2] published their major theoretical treatise on the absorption spectra of chromium(III) in ruby, a cornerstone in the development of crystal/ligand field theory. The ruby *R*-lines were then employed in the first successful demonstration of laser action by Maiman [3] at Hughes Aircraft Laboratories in 1960. In other milestones, Szabo [4] published the first observation of laser-based fluorescence line narrowing and transient spectral hole burning in a solid [5]. In the latter work, on 0.03 wt% ruby, Szabo observed that optical saturation also occurred for ions that were not resonant with the laser radiation and assigned this effect to cross relaxation in the $^4A_2$ ground state. This work was followed up and refined in a series of detailed investigations [6–10, and references therein]. Excitation energy transfer mechanisms and properties in ruby were also extensively investigated [11]. In another significant development, Macfarlane et al. [12] observed photon echoes in the superhyperfine limit in 14 ppm ruby. Finally, in a recent paper Bigelow et al. [13] purported the observation of ultraslow light propagation (group velocity of ca. 57 m/s) in ruby at room temperature. However, other researchers have shown that this latter observation can be interpreted by using a saturable absorber model without the need for group velocity reduction [14].

We have recently observed [15] conversion of side holes to anti holes in time-resolved transient spectral hole-burning experiments in low magnetic fields B$\|c$ in the chromium(III) $R_1$-line, $2\bar{A}(^2E) \leftarrow 2\bar{A}(^4A_2)$ of emerald, $Be_3Al_2Si_6O_{18}$:Cr(III) (0.0017 wt%), in the temperature

*Corresponding author. Tel.: +61 0 2 6268 86 79.
*E-mail address:* h.riesen@adfa.edu.au (H. Riesen).

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doi:10.1016/j.jlumin.2007.03.015

range of 3–12 K. Anti holes occur due to population storage in $^4A_2$ ground-state Zeeman levels; this population then decays only by spin-lattice relaxation in the ground state because cross relaxation is not effective in 0.0017% emerald.

The question then arises why this effect has not yet been reported for ruby, being an archetypal material in the spectroscopy of impurity ions in insulators. In particular, it is well documented that the spin-lattice relaxation time in ruby is about 200 ms at 4 K, and hence relatively long-lived spectral holes/anti holes can be expected. The present article addresses this question and demonstrates that, indeed, side-hole to anti-hole conversion is also observed in ruby, but a very low chromium(III) concentration of 0.6 ppm is required. Moreover, even in a 0.6 ppm sample cross relaxation between $^4A_2$ ground-state levels is only eliminated upon the application of low magnetic fields $B \| c$.

## 2. Experiment

Verneuil-grown boules of corundum crystals ($Al_2O_3$ nominal $<1$ ppm Cr(III)) and 20 ppm ruby (Djeva Ruby no. 1006) were obtained from Hrand Djevahirdjian SA, Monthey, Switzerland. Samples were cut and polished parallel and perpendicular to the crystal $c$-axis with diamond-impregnated tools. Crystal thicknesses of 6.8 and 8.8 mm were used for the 20 and $<1$ ppm crystals, respectively. From absorption experiments, we estimate that the corundum crystal contained about $0.6 \pm 0.2$ ppm chromium(III). The cut and polished samples were embedded using Cry-con grease on the cold finger of a closed-cycle cryostat (CCR, Janis/Sumitomo SHI-4.5). The inhomogenous linewidths of the $R_1(\pm\frac{3}{2})$ transition were about 10.6 and 6 GHz for the 20 and 0.6 ppm samples, respectively. These are 4–8 times wider than inhomogeneous widths observed in Czochralski-grown crystals. It is well documented that Verneuil-grown crystals usually display a significantly larger inhomogeneous width than Czochralski samples. The peak absorbance was 0.12 and ca. 0.008 for the 20 and 0.6 ppm samples, respectively.

Excited-state lifetime measurements were conducted by exciting the samples with modulated (acousto-optic modulator, Isomet 1205C-2) 532 nm light from a 10 mW Nd:YAG laser and observing the $R_1$-luminescence line through a Spex 1402 monochromator equipped with a 1200 grooves/mm holographic grating. The signal was measured by a photomultiplier (EMI 9785B), preamplified (Femto DLPCA-200 current–voltage preamplifier) and accumulated on a digital oscilloscope (LeCroy Wavesurfer 422).

The instrumental set-up for the transient spectral hole-burning experiments is described in detail elsewhere [15]. In brief, spectral holes were burnt and readout by a diode laser (Hitachi 6738MG, 35 mW, linewidth ca. 20 MHz as measured by a spectrum analyser with 300 MHz free spectral range) mounted in a thermoelectric mount (Thorlabs TCLDM9), driven by Thorlabs TEC2000 temperature and LDC500 current controllers. The laser light was passed through an external optical diode (Faraday isolator, EOT LD38I670), amplitude modulated by an acousto–optic modulator (Isomet 1205C-2), passed through an aperture and a linear polarizer (either polaroid film or Glan–Taylor calcite polarizer) and focussed on the sample using a 200 mm lens. The transmitted laser light was collimated and focussed by a 75 and 200 mm lens and detected by a photodiode (Thorlabs PDA55, 10 MHz bandwidth at minimum gain setting). The signal was processed by a digital storage oscilloscope (Le Croy Wavesurfer 422) and averaged waveforms (typically 512 averages in 11-bit-enhanced resolution mode) were transferred to a PC.

The sample was only exposed to laser light during the burn and readout periods. A (Master) pulse generator created the burn gate (ca. 200 μs) for the RF driver of the acousto–optic modulator. The Master triggered a second pulse generator (Slave 1), providing a delayed readout gate. Finally, Slave 1 triggered a waveform generator (Stanford Research Systems SRS DS345, Slave 2) that generated a synchronous modulation of the injection current of the diode laser by a triangular ramp, and thus a triangular modulation of the laser frequency. Ramp frequencies of 2500 Hz were used in the present experiments and the burn-read cycle was repeated at a rate of ca. 1 Hz. In comparison with the burn pulse (ca. 0.3 mW laser power), the readout light level was reduced by a factor of ca. 50. The instrumental resolution was about 20 MHz (laser linewidth limited) and $\approx$90 MHz for 5 and 30 GHz/200 μs scans, respectively, as determined by using the 300 MHz FSR etalon. The resolution of the 30 GHz/200 μs scans is lower because of several instrumental factors, including linearity ($\pm 0.5\%$) and repeatability of the voltage ramp provided by the SRS DS345 waveform generator.

The transverse magnetic field was generated by Helmholtz coils, arranged externally to the CCR. The coils provided a uniform magnetic field with a current dependence of 1.83 mT/A. Two power supplies (Hewlett Packard 6269 B) in series provided a current of up to 9 A at 80 V, yielding a maximum magnetic flux density $B$ of 16 mT. The dependence of the magnetic field strength on the current was calibrated using a Hall probe. The magnetic field was fairly homogeneous, varying less than 1% within the sample volume. The crystal $c$-axis was aligned with the direction of the external magnetic field using crossed polarizers, facilitating an alignment within $<2^\circ$.

For fields of 0.2 T two permanent magnets of 25 mm diameter were directly mounted on the sample holder of the CCR in "Helmholtz" configuration.

## 3. Results and discussion

Fig. 1 shows $\sigma$-polarized transient hole-burning spectra at 4 K for a 20 ppm ruby crystal in zero field and with an applied external field of $B \| c = 15$ mT. The laser was in resonance with the $R_1(\pm\frac{3}{2})$ line ($\bar{E}(^2E) \leftarrow 2\bar{A}(^4A_2)$), and the side hole observed at $-11.3$ GHz in zero field is due to the