

Persistent Spectral Hole-Burning in the R_1 Line of Cr^{3+} -Doped $\text{NaMg}[\text{Al}(\text{oxalate})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ Induced by Resonant Energy Transfer

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In the 3D network $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$ (ox = oxalate, bpy = 2,2'-bipyridine) phonon-assisted as well as resonant energy migration within the R_1 line of the $^4\text{A}_2 \rightarrow ^2\text{E}$ transition of Cr^{3+} has been identified. The latter is dominant below 4.2 K, and in a fluorescence line narrowing spectrum, it manifests itself in a multiline pattern across the inhomogeneous line width with spacings corresponding to the zero-field splitting of the $^4\text{A}_2$ ground state (Milos, M.; Kairouani, S.; Rabaste, S.; Hauser, A. *Coord. Chem. Rev.* **2008**, 252, 2540). H. Riesen demonstrated efficient spectral hole burning within the R_1 line of Cr^{3+} doped at low concentrations into partially deuterated $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$ (Riesen, H. *Coord. Chem. Rev.* **2006** 250, 1737). Here we show that at higher Cr^{3+} concentrations in the same host, both phenomena can be observed simultaneously, the resonant energy migration thus creating an additional series of persistent side holes.

1. Introduction

Spectral hole burning is a high-resolution site selective spectroscopy that can overcome some aspects of the inhomogeneous broadening, which obscures information regarding the electronic structure. Three different mechanisms of hole burning have been established to date:¹ photochemical hole burning, photophysical hole burning, and transient hole burning. The first mechanism involves a photochemical reaction upon the excitation of a subset of chromophores, and at the same time as the spectral hole is burnt, a photoproduct appears at quite different energy than the one of initially excited chromophores. Photophysical hole burning involves a rearrangement of host–guest interactions, and as a consequence, the initially excited subset of chromophores absorbs at slightly different energy but still within the inhomogeneous line width. Those two mechanisms result in persistent spectral holes. The third mechanism is, in principle, universal. Upon selective excitation of a subset of chromophores, a depletion of the ground state occurs at the laser frequency. This depletion lasts as long as the system takes to relax back to the initial ground state.

Persistent photophysical hole burning is rather common in amorphous systems at low temperatures,² but there are a few reports on photophysical hole burning in crystalline systems.^{3,4} One of the crystalline systems that exhibits persistent photophysical hole burning is Cr^{3+} -doped $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$ (ox = oxalate),⁵ in which Cr^{3+} substitutes for Al^{3+} . The photophysical and structural properties of this system have been studied extensively in the past.^{6–11} The crystal structure and, in particular, the number of water molecules in the lattice are crucial and have been well established.¹¹ Persistent photophysical holes can be burnt within the R_1 line of the $^4\text{A}_2 \rightarrow ^2\text{E}$ transition of Cr^{3+} . At a concentration of 1 mol %, the width of these holes in the absence of an external magnetic field is 20 MHz at 2.8 K and corresponds to the residual homogeneous line width limited by spin–spin relaxation.⁹ Partial deuteration of the water molecules increases the spectral hole burning efficiency by a factor of 1000 and leads to holes that are stable

up to 100 K.¹¹ The proposed mechanism is based on the rotational reorientation of water molecules of crystallization hydrogen bonded to oxalate around their pseudo- C_2 axes. When the DHO molecules undergo a 180° flip motion, the difference in the zero-point energies of the excited and ground state and hence the transition frequency changes. Thus, each photoinduced flip of a DHO molecules results in spectral hole-burning.¹⁰

Excitation energy transfer or energy migration within the R_1 line of the $^4\text{A}_2 \rightarrow ^2\text{E}$ transition of Cr^{3+} has been observed in a series of chromium tris-oxalate compounds,^{12–14} namely, in $[\text{Rh}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]\text{ClO}_4$ (bpy = 2,2'-bipyridine). In addition to the normally observed temperature-dependent phonon-assisted process, a resonant process between the zero-field split components of the $^4\text{A}_2$ ground state has been identified. The latter is dominant below 4.2 K, and in a fluorescence line narrowing (FLN) spectrum, it leads to a multiline pattern of sharp peaks spaced by the ground-state zero-field splitting (ZFS) across the inhomogeneous line width of the R_1 line. In contrast to doped $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$, the rigid oxalate networks show no persistent spectral hole burning.

In this article, we will show that at higher concentrations of Cr^{3+} in partially deuterated mixed crystals of $\text{NaMg}[\text{Al}_{1-x}\text{Cr}_x(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$, it is possible to burn simultaneously persistent holes and to observe resonant energy transfer, the latter in fact resulting in a series of additional persistent side holes.

2. Experimental Section

$\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$ and $\text{NaMg}[\text{Cr}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$ were prepared as described in the literature.¹⁵ Mixed crystals of $\text{NaMg}[\text{Al}_{1-x}\text{Cr}_x(\text{ox})_3] \cdot 9\text{H}_2\text{O}$ were grown by slow evaporation from aqueous solutions containing given fractions of $[\text{Al}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{ox})_3]^{3-}$. The effective Cr^{3+} concentrations in the crystals were determined from single crystal absorption spectra. Partially deuterated crystals were grown from solutions containing the desired ratio of $\text{H}_2\text{O}/\text{D}_2\text{O}$. Crystals of the following compositions were used in the present study: protonated $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$, partially deuterated

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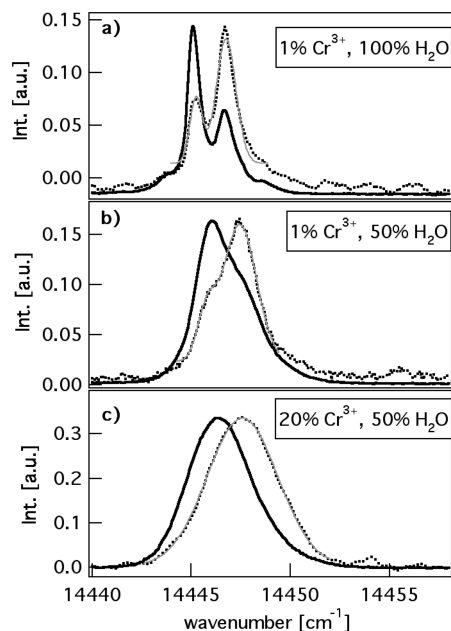


Figure 1. Absorption (···) and nonselectively excited luminescence (—) in the region of the R_1 lines of the $^4A_2 \rightarrow ^2E$ transition of $[\text{Cr}(\text{ox})_3]^{3-}$ in different lattices at 1.4 K: (a) $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$, (b) $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$, and (c) $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$.

$\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$, and $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$, the latter both with a $\text{H}_2\text{O}/\text{D}_2\text{O}$ ratio of 1:1.

The samples were cooled to 1.4 K in a helium bath cryostat (Cryo Industries). Conventional transmission spectra were measured by passing white light from a tungsten lamp through a band-pass filter (50 nm band path at 700 nm) and analyzing the transmitted light using a double monochromator (SPEx 1403) and a CCD camera (Roper Instruments), giving a spectral resolution of 0.25 cm^{-1} . For nonselective luminescence spectra, samples were excited at 532 nm , that is, into the $^4A_2 \rightarrow ^4T_2$ transition of Cr^{3+} , from an intracavity frequency doubled Nd/YAG laser (ILEE VA-I-N-532). FLN spectra were obtained by selective excitation using a single frequency Ti/sapphire laser (Coherent 699) at $\sim 14\,450 \text{ cm}^{-1}$, that is, within the R_1 electronic origin of Cr^{3+} . The collected emission was dispersed by the same monochromator and detected by the same CCD camera as above. Persistent photophysical holes were burnt with the same Ti/sapphire laser for 40 min and with a laser power of 5 mW/mm^2 for optimum results. The spectral holes were observed in absorption and luminescence spectra using the same detection setup, and in both cases, the irradiation power was reduced with gray filters to avoid heating of the sample and to reduce photophysical hole filling.

3. Results and Discussion

Figure 1a,b shows the absorption and nonselectively excited luminescence spectra in the region of the R_1 line of the $^4A_2 \rightarrow ^2E$ transition at 1.4 K for the dilute samples of this study, namely, $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9\text{H}_2\text{O}$, and partially deuterated $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$. In the fully protonated system, the inhomogeneous line widths of the two components of the transition are $\sim 0.8 \text{ cm}^{-1}$, and the ground-state ZFS of $D = 1.6 \text{ cm}^{-1}$ is fully resolved and in agreement with EPR and FLN spectroscopy.^{5,6} Partially deuterating the system broadens both components of the R_1 line, and consequently, the inhomogeneous line widths is $\sim 1.7 \text{ cm}^{-1}$. For the latter, the ground-state ZFS is thus barely discernible as shoulder in both

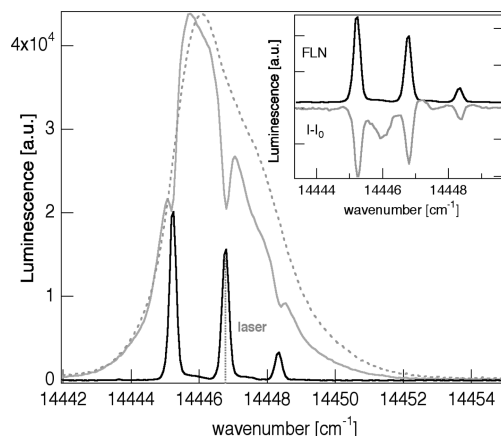


Figure 2. FLN spectrum (—) and nonselectively excited luminescence spectrum before (···) and after spectral hole burning (gray line) of $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ at 1.4 K. Inset: difference in nonselectively excited luminescence before (I_0) and after hole burning (I) together with the FLN spectrum.

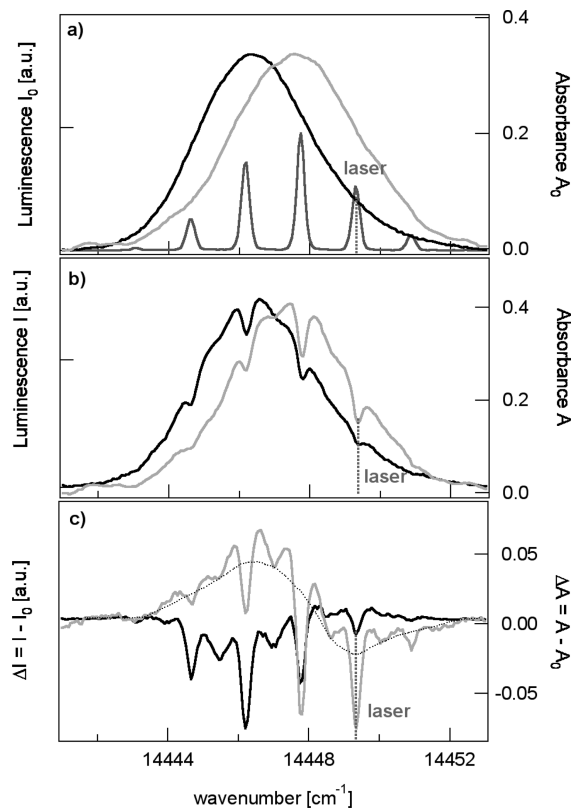


Figure 3. (a) Absorption (gray line), nonselectively excited luminescence before hole burning (—), and FLN (dark gray line) spectrum of the R_1 transition of Cr^{3+} in $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ at 1.4 K. The FLN spectrum is obtained with selective excitation at $14\,449.3 \text{ cm}^{-1}$, which is within the R_1 absorption. (b) Nonselectively excited luminescence (—) and absorption (gray line) spectrum after hole burning at $14\,449.3 \text{ cm}^{-1}$. (c) Difference luminescence (—) and absorption (gray line) spectra before and after hole burning at $14\,449.3 \text{ cm}^{-1}$ and (···) guide for the eye illustrating the contribution of phonon-assisted energy transfer to the difference absorption spectrum.

absorption and emission spectra. The intensity ratios of the zero-field split components in absorption and emission for both samples are in agreement with the $\pm 3/2$ component of the 4A_2 state being below the $\pm 1/2$ component.^{16,17}

Figure 1c shows the absorption and nonselectively excited luminescence spectra at 1.4 K of the more concentrated system

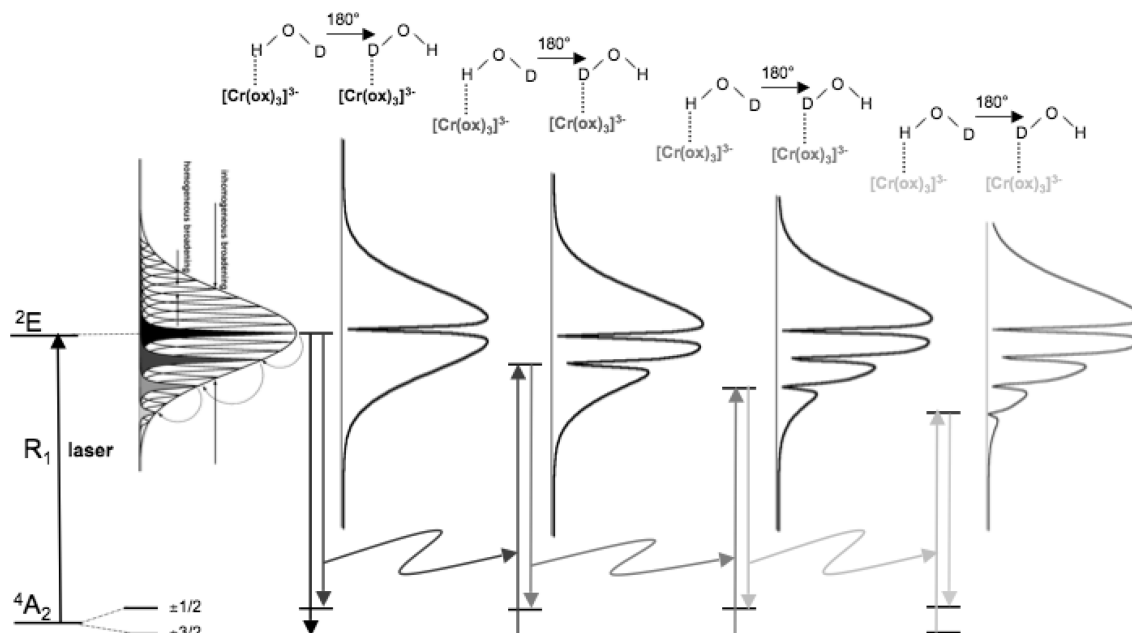


Figure 4. Scheme for the persistent hole burning induced by nonradiative resonant energy transfer within the R_1 line of Cr^{3+} in $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$.

of this study, namely, $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$. With 4.2 cm^{-1} , the inhomogeneous broadening of the $\pm 3/2$ and $\pm 1/2$ components of the R_1 line of this sample is large enough such that the ground-state ZFS is not resolved. There is, however, another difference compared with the more dilute samples: whereas the Stokes shift for the compounds containing 1% of Cr^{3+} is close to zero, the Stokes shift for the sample containing 20% Cr^{3+} is $\sim 2 \text{ cm}^{-1}$, as a first indication for energy migration at higher Cr^{3+} concentrations.

The FLN spectrum presented in Figure 2 on dilute but partially deuterated $\text{NaMg}[\text{Al}_{0.99}\text{Cr}_{0.01}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ shows the typical three-line spectrum characteristic for isolated Cr^{3+} chromophores, with the central line at the laser frequency of $14\,446.8 \text{ cm}^{-1}$ and the satellite lines at $\pm D$ from the resonant line.¹³ In accordance with ref 5, persistent holes were burnt in this system by selectively irradiating at $14\,446.8 \text{ cm}^{-1}$ for 40 min and with 5 mW/mm^2 laser power. As expected and shown in Figure 2, three holes are observed in the subsequently recorded nonselectively excited luminescence spectrum, that is, the resonant hole at $14\,446.8 \text{ cm}^{-1}$ and the side holes at $\pm D$. Because the excitation was performed in the middle of the absorption band, there are fewer chromophores that contribute to the luminescence spectrum. This also explains the difference between nonselectively excited luminescence spectra before and after spectral hole burning at the red wing of the band. It should be noted that in Figure 2, the hole width is limited by the spectral resolution of the monochromator of 0.25 cm^{-1} . This is several orders of magnitude $>20 \text{ MHz}$ of the homogeneous line width, as determined by Riesen et al.⁹ in dilute systems at the same temperature and the 600 MHz as upper limit for more concentrated systems.¹³ However, in the context of the present study this is not important.

For the more concentrated sample, $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$, both FLN and spectral hole burning give very different results compared with the diluted systems. In addition to the absorption and nonselectively excited luminescence, Figure 3a shows the FLN spectrum of $\text{NaMg}[\text{Al}_{0.8}\text{Cr}_{0.2}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ upon excitation at $14\,449.3 \text{ cm}^{-1}$ with low laser power. Instead of the three lines, the FLN spectrum consists of six lines separated by the ground-state ZFS. As for the diluted sample,

the laser excites a subset of chromophores inside the inhomogeneously broadened R_1 line of the $^4A_2 \rightarrow ^2E$ transition having a transition energy within a homogeneous line width around the excitation energy. In addition to returning back to the ground state by luminescence, and as schematically shown in Figure 4, in the more concentrated sample, the initially excited chromophore can transfer its energy resonantly to a subset of chromophores within the R_1 line that are separated by the ground-state ZFS. The thus excited chromophore will, in turn, emit at $-D$ and $-2D$ from the laser line or transfer its energy resonantly to a subsequent chromophore again at $-D$ lower in energy. Repetitive resonant energy transfer thus results in the observed multiline pattern. The fact that the line resonant with the laser line carries only $\sim 15\%$ of the total luminescence intensity indicates that the energy transfer rate constant is 5 to 10 times larger than the radiative decay rate constant of $k_r = 700 \text{ s}^{-1}$ ($\tau_r = 1.3 \text{ ms}$).¹³

Figure 3b shows the nonselectively excited luminescence and absorption spectrum of the R_1 line after irradiation during 40 min at $14\,449.3 \text{ cm}^{-1}$ and 5 mW/mm^2 of the more concentrated sample. It is evident that the irradiation has burnt persistent holes, not only at the laser energy and the satellites at $\pm D$ from the resonant line but also for all peaks of the multiline pattern of the corresponding FLN spectrum.

To enhance the holes visually, Figure 3c shows the difference luminescence spectrum $\Delta I = I - I_0$ of the luminescence before (I_0) and after (I) irradiation at $14\,449.3 \text{ cm}^{-1}$ as well as the corresponding difference absorption spectrum $\Delta A = A - A_0$. The intensity distribution of the actual holes closely follows the intensity distribution of the peaks in the FLN spectrum, indicating that they are indeed burnt by the resonant energy transfer or cross relaxation process and not by emission and reabsorption. The guide for the eye on the difference absorbance spectrum in Figure 3c shows that there are two different types of photoproduct from the hole burning. On both sides of each hole rise well-known selective photoproducts that are directly related to the holes burnt by resonant energy transfer. However, there are nonselective, randomly distributed photoproducts that manifest themselves as a broad nonselective shift of absorption intensity to lower energies compared with the excitation energy.

This second type of photoproduct can be related to photoproducts created by nonselective phonon assisted energy transfer.

4. Conclusions

As shown by Riesen et al. in $\text{NaMg}[\text{Al}_{1-x}\text{Cr}_x(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$ efficient persistent hole burning is due to the deuteration effect, the photoinduced $\text{HOD} \rightarrow \text{DOH}$ flip of hydrogen bonded water molecules being responsible for the shift in absorption energy of the selectively excited chromophores. With 20% concentration of Cr^{3+} in $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 9(\text{H}_2\text{O}/\text{D}_2\text{O})$, the resonant energy migration within the R_1 line of Cr^{3+} is efficient, and in the FLN spectrum, it manifests itself as a multi line pattern with six members. In the present article, we showed that it is possible to combine both phenomena and burn not only persistent resonant and side holes of the initially excited chromophore, but also resonant energy transfer or cross-relaxation-induced holes. In addition, we showed that there are two types of photoproducts resulting from energy transfer. The first type of photoproducts appears selectively on both sides of the spectral holes and are directly related to the resonant energy transfer. The second type of photoproducts are the nonselective ones that appear as a broadband shifted to lower energies compared with the excitation energy and which are related to the phonon-assisted energy transfer. The 20% Cr^{3+} concentration proved to be optimal for the observation of the energy selective multiline side hole burning because at that concentration, the inhomogeneous line width is sufficiently large to accommodate several members of the multiline pattern spaced by the ZFS of the ground state, and the resonant energy migration is efficient enough to result in the typical multiline pattern, whereas at higher concentrations, the energy migration becomes so fast that the selectivity is lost as a result of spectral diffusion because of quasi-resonant migration.¹⁸

In the present system, donor and acceptor are chemically identical, but the above concept of persistent spectral hole burning via resonant energy transfer or cross relaxation involving inhomogeneously broadened electronic origins should likewise be possible for chemically different donor–acceptor pairs, for instance, in combination with lanthanide-based systems.

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