High-resolution spectroscopy and optical hole burning studies of the $^7F_0 \rightarrow {}^5D_0$ transition of europium-doped calcium fluoride

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High-resolution spectroscopic study of the $^7F_0 \rightarrow {}^5D_0$ transition revealed more than 40 different sites for the rare-earth ion. The multisite behavior was found to be due to clustering of the dopants and dopant induced microscopic defects. Hole-burning efficiencies were measured for some sites. © *2000 American Institute of Physics.* [S0021-8979(00)02607-4]

Calcium fluoride is a cubic material. Rare-earth ions were known to occupy different sites due to charge compensation. Hamers *et al.*[1] identified five different sites in $CaF_2:Eu^{3+}$ (0.1%) whose $^7F_0 \rightarrow {}^5D_0$ absorption wavelengths fall at 579±0.6 nm. High-resolution spectral studies were also performed on these materials by the hole-burning technique. Hole-burning studies of the tetragonal site[2] and oxygen-compensated trigonal site were performed in the past.[3–5] Hole burning was also pursued in several other europium-doped crystals and glasses.[6–10] The $^5D_0$ and $^7F_0$ states of Eu^{3+} are singlets in the crystal field. A transition between these two states is expected to reveal a single peak either in absorption or emission, in defect free perfect crystals. A recent investigation[11] on the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} doped Y_2SiO_5 revealed more than 40 different satellite lines for the dopant though the prior studies revealed only two sites.[12] Similar observations were made in $EuVO_4$[13] and $YAlO_3:Eu^{3+}$[14] also. The satellite lines were ascribed to ions that were on the sites differently perturbed, by defects or clustering of Eu^{3+} ions. It is not clear yet whether this multisite behavior is universal or dependent on the host material. So, we reinvestigated the high-resolution spectroscopy and hole-burning phenomena in $CaF_2:Eu^{3+}$. Our studies revealed more than 40 different sites for the Eu^{3+} ion whose transition wavelengths ($^7F_0 \rightarrow {}^5D_0$) fall within 1 nm centered around 579.5 nm.

The sample is of size $0.8 \times 0.6 \times 0.4$ cm^3 and was obtained from Optovac, Inc. The concentration of the dopant is 0.5 mol %. Absorption spectrum was recorded by a Varian-CARY3E spectrophotometer. A high-resolution ring-dye laser of linewidth ~3 MHz and a low-resolution dye laser of linewidth ~60 GHz were used to excite the samples. The sample was cooled to 9 K in a closed cycle cryostat for all the emission and excitation measurements. The emission was processed by a medium resolution spectrometer that has a dispersion of 1.7 nm/mm. In some high-resolution excitation measurements the slitwidth limited bandpass of the instrument was about 5 nm. The light was detected by a Hamamatsu Model R928 photomultiplier tube. Its output was amplified and plotted on a chart recorder. In high-resolution excitation spectral measurements the amplified

signal was given to a storage oscilloscope whose output was plotted on an $X-Y$ recorder. The use of a spectrometer simplifies the analysis of different sites. The ring dye laser was operated in the free running mode for recording the high-resolution excitation spectra and in the stablock mode for burning and recording spectral holes. The laser wavelengths were measured by a Coherent–Ealing wavemeter, Model 33-2684.

Absorption spectrum revealed two strong peaks centered at 230 and 360 nm, which are very broad when compared to the Eu^{3+} transitions. These wavelengths are in close agreement with the Eu^{2+} transitions.[1] Fluorescence spectrum was recorded by resonantly exciting the $^5D_0$ level. Emission occurred at 579, 590, 617, 650, and 701 nm to different ^7F_J levels ($J=0-4$). Strong emission occurred at 590 and very weak emission occurred at 650 nm. The emission intensity and the number of peaks in any group varied dramatically depending on the laser wavelength used (or site that was excited). Emission from all the sites overlapped at 593.7 nm. A low resolution excitation spectrum of 593.7 nm revealed about 21 peaks, in the wavelength interval 577–581 nm, suggesting that there are at least 21 different sites for the rare-earth ion. There are marked differences in the emission spectral characteristics whenever the laser excitation wavelength was tuned slightly within the wavelength interval 579.6–580.2 nm. This indicates that all the excitation peaks represent different sites of the dopant. However, a high-resolution excitation spectrum revealed about 42 peaks in the wavelength interval 579–580 nm (Fig. 1). The low-resolution excitation spectrum was recorded with a laser whose linewidth is ~60 GHz. So, some of the closely spaced peaks were not separated. The high-resolution spectrum was recorded by operating the ring dye laser in the free running mode whose linewidth is ~15 MHz. As a result, we were able to detect more than 40 peaks in the high-resolution excitation spectrum whose wavelengths fall within 1 nm of the central wavelength. High-resolution excitation spectra were recorded in several overlapping segments with each segment covering ~40 GHz. The strongest peaks were peak No. 5, at 579.9 (579.412 nm) and peak No. 31, at 579.0 nm (578.446 nm) and the numbers given in the parentheses are those reported by Hamers *et al.*[1] The intensity of any other peak is ~10× less than that of the strongest peak. There is some
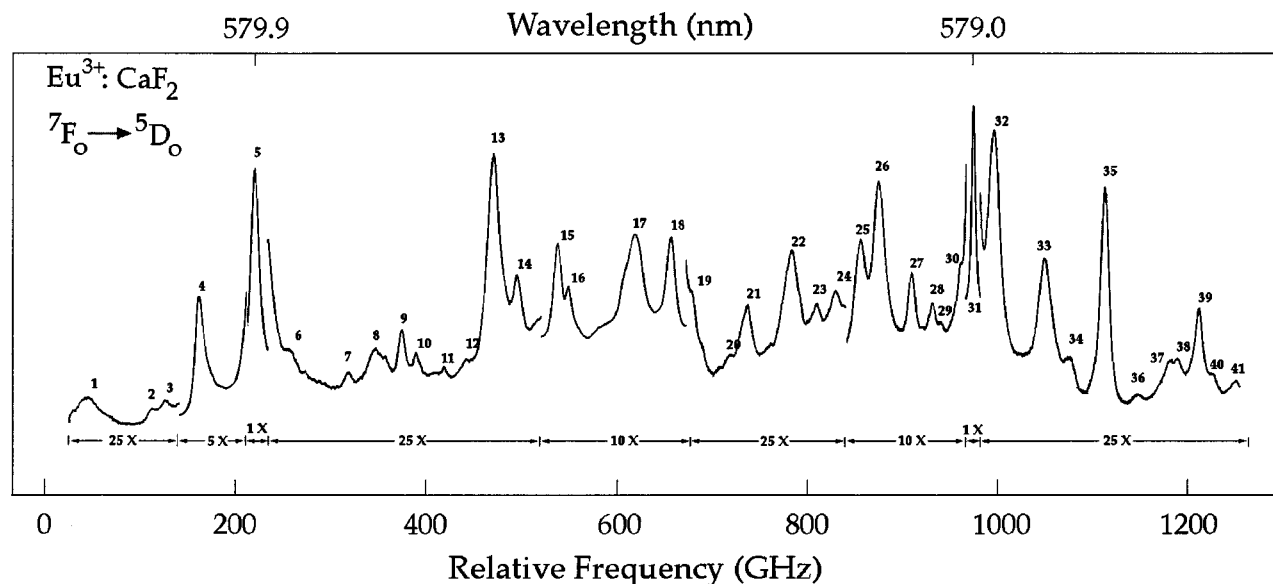

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FIG. 1. High-resolution spectrum of the $^7F_0 \rightarrow ^5D_0$ transition of CaF_2:Eu^{3+}. The excitation spectrum was recorded by monitoring emission at 593.7 nm.

discrepancy between the wavelengths measured by the wavemeter (in the present case) and those reported by Hamers *et al.*[1] However the wavelength interval between the strong peaks is comparable.

All the peaks shown in Fig. 1 represent electronic levels of different sites and not phonon-coupled levels. This was confirmed by recording the hole-burning spectra for all the peaks (or sites). Hole formation was also verified by recording the temporal evolution of the emission intensity for all the peaks. Holes were burnt in the absorption spectrum by exposing the sample to about 20 mW of laser radiation for about 20 s. Excitation spectrum was recorded by sweeping the same laser frequency at reduced power. A 1 GHz scan was completed in less than 2 s. For some peaks, a recording of the hole spectrum revealed side holes and antiholes also (Fig. 2). Analysis of the hole-burning spectra revealed that each satellite peak has its own hyperfine splittings indicating that they all represent electronic levels. Some of the holes are long lived at 9 K. The hole lifetime varied from 3 min (longest for peak No. 5) to 10 s (least for peak No. 27), for all the other peaks the hole lifetimes are in between. The ionic concentration is 1.225×10^{20} cm^{-3}. Integrated absorption measurements revealed that about half of the ions contributed to the formation of the two strong peaks Nos. 5 and 31. Hole-burning efficiency was estimated by using the procedure given elsewhere.[15] Based on relative estimates, it was found that peak No. 31 exhibited the highest hole burning efficiency and peak No. 39 the lowest, and the efficiency was in between for all the other peaks. The efficiency of peak No. 5 is about 27% less than that of peak No. 31. The total inhomogeneous broadening of all the sites was estimated as ~ 410 GHz (full width at half maximum).

In a 0.1% sample Hamers *et al.*[1] observed only about five dominant sites. However, in a 0.5% sample the number of sites were found to be 20 under low-resolution measurements and 42 under high-resolution measurements. This indicates that the multisite behavior is predominantly due to clustering of the dopant ions and the presence of microscopic defects induced by the dopants in the crystal. Our results indicate that this effect is universal and should be observable in all the materials. However, this effect was not detected in the $^3H_4 \rightarrow ^1D_2$ transitions of Pr^{3+} doped materials[16] because of the occurrence of a strong absorption to the neighboring Stark levels.
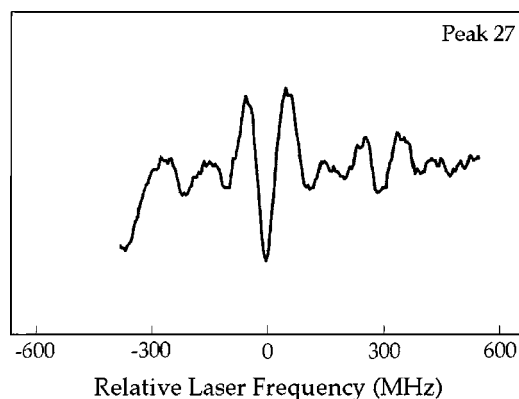
FIG. 2. Hole-burning spectrum for peak No. 27 of Fig. 1. The transition is $^7F_0 \rightarrow ^5D_0$.

[1] R. J. Hamers, J. R. Wietfeldt, and J. C. Wright, J. Chem. Phys. **77**, 683 (1982).
[2] A. J. Silversmith and R. M. Macfarlane, Phys. Rev. B **45**, 5811 (1992).
[3] A. P. Radlinski and A. J. Silversmith, Phys. Rev. B **34**, 86 (1986).
[4] A. J. Silversmith and N. B. Manson, Phys. Rev. B **34**, 4854 (1986).
[5] A. J. Silversmith, A. P. Radlinski, and N. B. Manson, Phys. Rev. B **34**, 7554 (1986).
[6] K. Fujita, K. Tanaka, K. Hirao, and N. Soga, Opt. Lett. **23**, 543 (1998).
[7] Y. Mao, P. Gavrilovic, S. Singh, A. Bruce, and W. H. Grodkiewicz, Appl. Phys. Lett. **68**, 3677 (1996).
[8] D. M. Boye, Y. Sun, and R. S. Meltzer, J. Lumin. **66&67**, 184 (1996).
[9] K. Koyama and T. Suemoto, J. Lumin. **66&67**, 164 (1996).

[10] L. E. Erickson and K. K. Sharma, Phys. Rev. B **24**, 3697 (1981).

[11] R. S. Pandher, A. Jackson, A. Davis, and B. R. Reddy, Appl. Opt. **38**, 5662 (1999).

[12] R. Yano, M. Mitsunaga, and N. Uesugi, J. Opt. Soc. Am. B **9**, 992 (1992).

[13] M. Yamaguchi, K. Koyama, T. Suemoto, and M. Mitsunaga, J. Lumin. **76&77**, 681 (1998).

[14] R. L. Cone, P. C. Hansen, and M. J. M. Leask, J. Opt. Soc. Am. B **9**, 779 (1992).

[15] W. E. Moerner, M. Gerhtz, and A. L. Huston, J. Phys. Chem. **88**, 6459 (1984).

[16] R. M. Macfarlane, in *Persistent Spectral Hole Burning: Science and Applications*, Topics in Current Physics, Vol. 44, edited by W. E. Moerner (Springer, New York, 1988).