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Gamma-ray-induced color in CaF_2 at room temperature: Coloring kinetics and thermal annealing

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The coloring curves of the optical-absorption bands at 227, 336, 395, and 575 nm induced by γ irradiation in natural and Harshaw fluorite single crystals at room temperature have been obtained. Like the *F* coloring curves in alkali halides, they show three coloring stages. The dose-rate effect on these coloring curves has also been studied. It has been found that there is a constant ratio between the optical density at 336 nm and the optical density at 395 nm throughout the whole range of irradiation dose used to obtain the coloring curves. This ratio is the same in both types of samples and it is independent of the irradiation dose rate. There is not proportionality among the other absorption bands. From isothermal annealing measurements between 125 and 330 °C the pre-exponential factors and the activation energies of the annealing processes have been obtained. These results are discussed in relation with the current models of color centers for these optical bands in CaF_2.

I. INTRODUCTION

The coloring properties of calcium fluoride were known many years ago.[1] The color induced by ionizing radiation has been studied under a large variety of experimental conditions,[2–4] such as impurity doping, irradiation temperature, etc. The number of optical-absorption bands that can be produced in CaF_2 by irradiation is larger than in the well-studied alkali halides. Moreover, since CaF_2 is harder to color than the alkali halides, the information available about the coloring kinetics of those absorption bands induced by irradiation is small.

Early measurements of the optical-absorption spectrum induced by x irradiation of natural and synthetic single crystals of CaF_2[5–8] show the formation of four absorption bands at 580, 400, 335, and 225 nm. At that time, it was concluded that these absorption bands were due to intrinsic rather than impurity-related color centers. However, it was later proposed[9] that the four bands are electronic transitions of the Y^{2+} ion produced in the sample by the radiation-induced reduction of the Y^{3+} ion which is always present as a contaminant in natural fluorite. Another model has been recently proposed[10–12] in which the four-band spectrum is assigned to a single anisotropic color center formed by a trivalent-rare-earth ion associated with a fluorine vacancy, with two electrons trapped at this complex defect.

The purpose of the work reported in this paper was to obtain careful coloring curves—optical density versus dose—of the radiation-induced four absorption bands and to study the thermal stability of these bands, since to our knowledge the information available on both points is meager. Also, it was expected to see how these results fit with the proposal of a single center as the origin of the four-absorption-band spectrum.

II. EXPERIMENTAL

Square samples 1.5×1.5 cm^2 and between 0.6 and 1.5 mm were cleaved from a Harshaw single-crystal block of CaF_2 or from natural single crystals obtained from the mining works at Caravia (Asturias, Spain). The samples were polished down to the desired thickness. Prior to irradiation, they were annealed in vacuum at 450 °C for 3 h and then slowly cooled to room temperature. The samples were irradiated at room temperature with γ rays from a ^{60}Co source.

After irradiation, the optical-absorption spectrum was measured with a Perkin Elmer 350 spectrophotometer. The sample was mounted in a small furnace within the cell of the spectrophotometer in order to record the thermal bleaching at a fixed wavelength while the temperature of the sample is kept constant within 1 °C. The range of temperature was between 120 and 330 °C.

III. RESULTS

A. Coloring curves

The same optical-absorption bands with maxima at 575, 393, 336, and 227 nm are induced by γ irradiation in natural and Harshaw samples. With increasing radiation dose the absorption peak initially at 575 nm shifts towards 560 nm, while the absorption peak at 395 nm moves slowly up to 397 nm. The coloring curves of these two bands were obtained measuring the optical density at their absorption maxima without taking into account the indicated displacements. There is also another optical-absorption band with its maximum at wavelengths shorter than the uv limit of the spectrophotometer.[5,6] This band was monitored by measuring the optical density at 195 nm. It was also found that at high-radiation dose, small absorption bands appear at 780 and 1025 nm in both Harshaw and natural samples. The absorption peak initially at 1025 nm shifts to larger wavelength as the dose is increased. The difference between an optical spectrum at high-radiation dose and another at low-radiation dose clearly shows the formation of small absorption bands with maxima at 262, 365, and 490 nm. These bands introduce small errors in the values of the optical densities used to obtain the coloring curves of the bands initially at 227, 336, 395, and 575 nm, so no overlap corrections were made.

Figure 1 shows the coloring curves—optical density versus dose—corresponding to the optical-absorption bands at 227, 336, 395, 575, and 1025 nm and to the optical absorption at 195 nm, in natural single crystals of CaF_2 irradiated at a dose rate of 3.6×10^6 R/h. Except for the band at 1025 nm, three growth stages are clearly observed. As in the *F* coloring curve in alkali halides,[2] there is a fast initial stage of coloring, then a linear stage, and finally at high-radiation dose, a fast third stage appears. The band at 1025 nm increases continuously with the irradiation dose in a way that recalls the coloring curve of the *M* center in alkali halides. The inset of Fig. 1 shows in detail the fast initial stage of the coloring curves as well as the dose-rate effect on these curves. After a point on the linear stage of coloring is reached with an irradiation dose rate of 3.6×10^6 R/h, the dose rate is decreased down to 0.6×10^6 R/h. The coloring curves of the bands at 195, 227, 336, and 395 nm show a dip; afterwards, the irradiation dose rate is again increased to 3.6×10^6 R/h, these bands then grow in such a way that the initial trend of coloring is restored. This is analogous to the dependence of the *F* coloring curve on the dose rate in alkali halides.[13] The coloring curve corresponding to the band at 575 nm does not show any dependence on the radiation dose rate. Since the band at 1025 nm is very small, the dependence on the dose rate of the corresponding coloring curve was not studied. Except for this last band, Fig. 2 shows the coloring curves obtained in Harshaw samples corresponding to the other absorption bands. They were also irradiated at 3.6×10^6 R/h. The colorability is lower than in the natural samples; however, the same three coloring stages are clearly observed.

In order to find out if the dependence on the dose rate of the coloring curves is already operative during the first coloring stage, the coloring curves at a dose rate of 0.6×10^6 R/h were measured. It was also found that in the first coloring stage the lower the dose rate the smaller optical density for the same dose. Figures 3 and 4 show these coloring curves for natural and Harshaw samples, respectively. With this low-radiation dose rate it is not viable to reach the third coloring stage or even to get a well-defined linear stage due to the long irradiation time that has to be used.

Since these radiation-induced absorption bands at 227, 336, 395, and 575 nm have been attributed to a *single* color center, either a Y^{2+} substitutional ion[9] or to a *F* center associated with a divalent rare-earth impurity,[10–12] it is sensible to find out

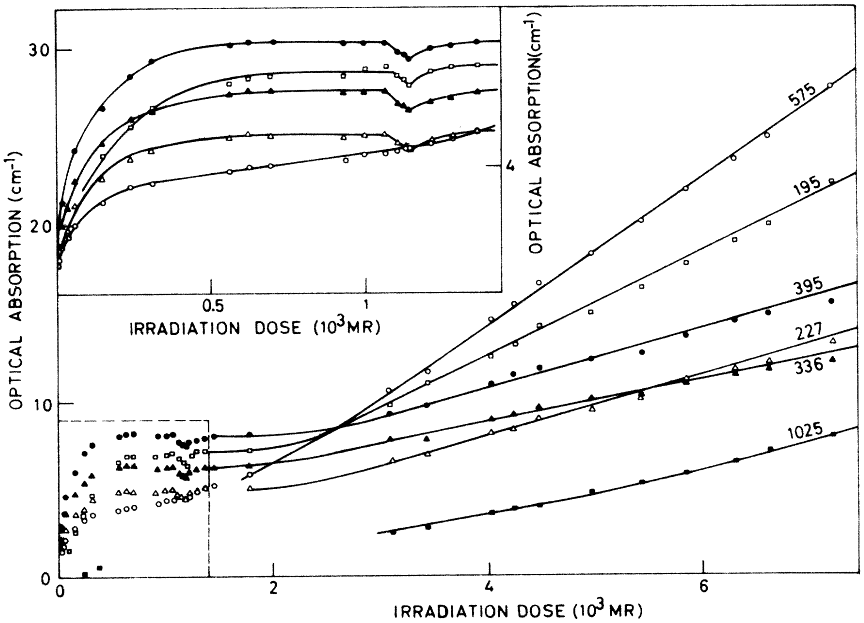

FIG. 1. Coloring curves in natural fluorite single crystals γ irradiated at a dose rate of 3.6×10^6 R/h. The number on each curve is the wavelength (nm) at the maximum of the corresponding absorption band. The inset details the first coloring stage and the dose-rate effect.

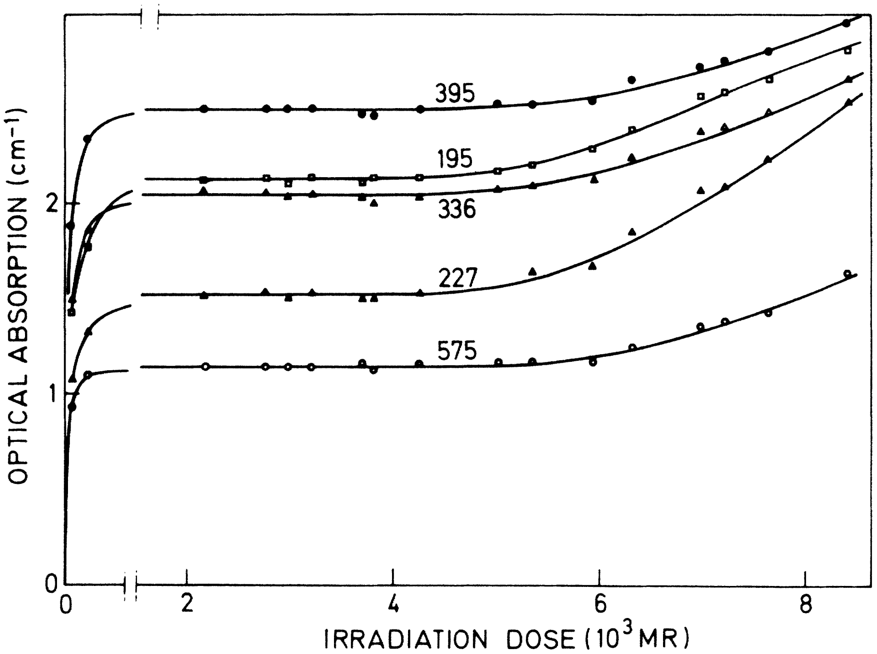

FIG. 2. Coloring curves in Harshaw fluorite single crystals γ irradiated at a dose rate of 3.6×10^6 R/h. The number on each curve is the wavelength (nm) at the maximum of the corresponding absorption band. Note that the irradiation-dose axis is broken in order to show the onset of the third coloring stage.

whether the optical densities of these bands grow proportionally throughout the whole range of dose used to obtain the coloring curves. It was found that only the optical densities of the bands at 336 and 395 nm were always proportional. This ratio is independent of the dose rate and it is the same in natural and Harshaw samples, as shown in Fig. 5. No any other simple relation was found among the coloring curves of these bands, except for a quadratic relation between the bands at 395 and 1025 nm as can be seen in Fig. 5.

Optical bleaching with unfiltered light from a 450-W xenon lamp produces a proportional reduction of all the absorption bands. Some bleaching experiments were done with filtered light adecuated to each of the bands at 227, 336, 395, and 575 nm. The results were small and erratic changes of the optical-absorption spectrum.

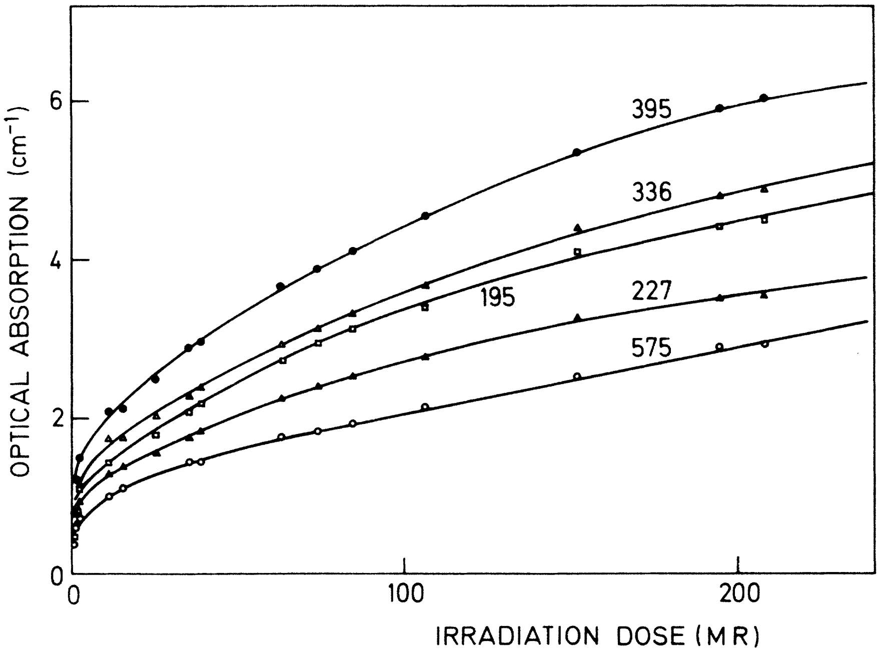

FIG. 3. Coloring curves corresponding to those in Fig. 1, obtained at 0.6 R/h.

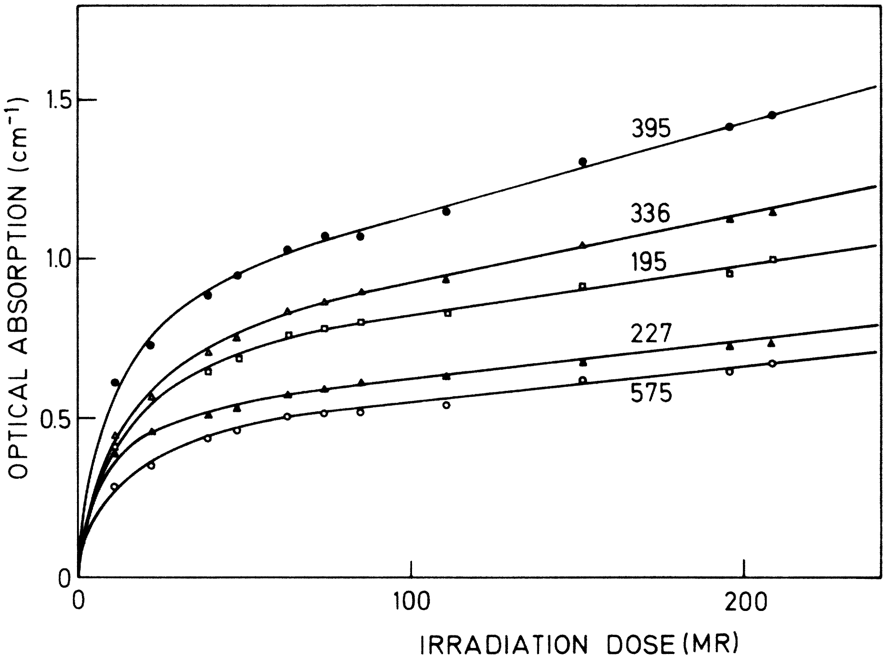

FIG. 4. Coloring curves corresponding to those in Fig. 2, obtained at 0.6 R/h.

B. Thermal bleaching

Figure 6 shows the annealing of the optical-absorption band at 336 nm while the temperature of the sample is increased at a constant rate of 15 °C/min. Under identical experimental conditions, the same annealing curve is obtained for the other absorption bands. Two clear annealing steps with inflection points at 196 and 308 °C appear. There is also a poorly resolved annealing step at a 230 °C. It was observed that annealing treatments prior to the heating run induce changes in the temperatures at which the annealing steps occur. It was thought that the annealing of the absorption bands is more complex than Fig. 6 shows. Thus, a careful isothermal-annealing study at temperatures between 125 and 330 °C was made for each of the four bands. It was found that the isothermal-annealing curves are a superposition of several exponential decays up to a maximum of five depending on the annealing temperature. The lifetimes τ_i of these exponential decays depend on the temperature in the form

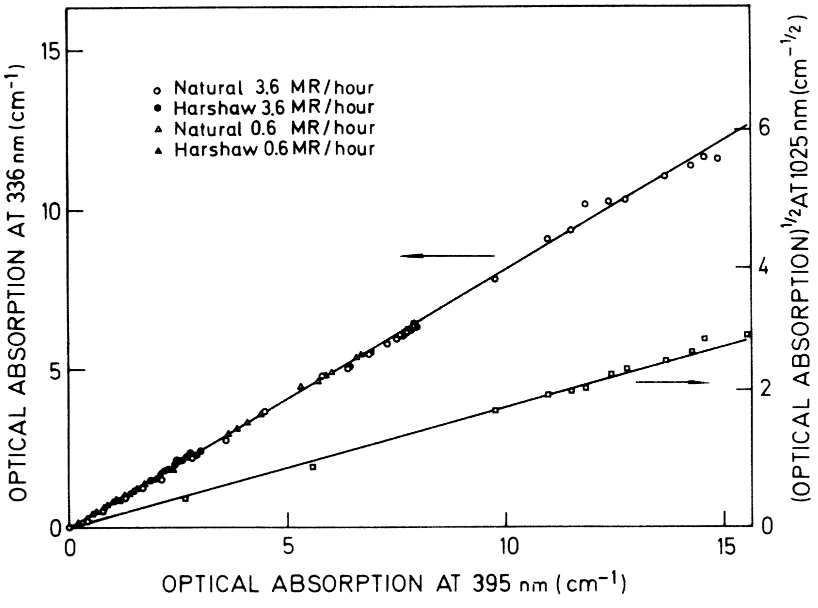

FIG. 5. Linear relation between the optical density at 336 nm and the optical density at 395 nm. The empty squares represent the quadratic relation between the optical density at 395 nm and the optical density at 1025 nm.

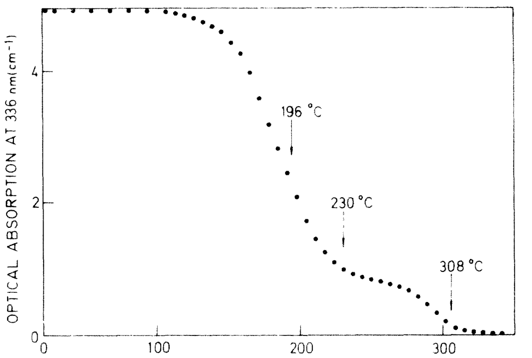

FIG. 6. Thermal annealing of the absorption band at 336 nm. The sample was heated at 15 °C/min.

$1/\tau_i = S_i e^{E_i/kT}$, where S_i is a temperature-independent pre-exponential factor, E_i is the activation energy, k is the Boltzmann constant, and T is the absolute temperature.

It was found that the four absorption bands at 227, 336, 395, and 575 nm, as well as the optical density at 195 nm, follow the same annealing kinetics with the same pre-exponential factors and activation energies. Table I summarizes these experimental results.

IV. DISCUSSION AND CONCLUSIONS

We have presented a detailed study of the coloring curves of γ-induced optical-absorption bands and of the thermal stability of these bands. The shape of the coloring curves, Figs. 1 and 2, with three stages of growth is not in agreement with the Y^{2+} substitutional-ion model.[9] In this model, the coloring curves should reach, after a more or less fast initial stage, a saturation level depending on the radiation dose rate and/or the Y^{3+}-ion concentration,[9] but a fast third stage of coloring should not be expected. The coloring curves obtained can be in agreement with the formation of intrinsic centers (vacancies or interstitials) or centers with an intrinsic component as in the model[10–12] in which a vacancy is associated with a trivalent-rare-earth ion. The explanation of the three stages in the coloring curves can be quite analogous to the *F* coloring curves in alkali halides.[14]

It was found that, while there is always a constant ratio, independent of the type of sample and dose rate, between the optical densities at 336 and 395 nm, the optical density at 575 nm is not proportional to the optical densities of those bands throughout the whole range of radiation dose used to obtain the coloring curves. Only at low dose may it be said that all these bands are proportional to each other. By subtracting corresponding absorption spectra at different doses, small absorption bands were found under the main bands. Since they are very small the contribution of these hidden bands can not be the reason why the band at 575 nm does not grow proportional to the bands at 336 and 395 nm. We also studied the dose dependence of the ratio between the optical density at 395 nm and the optical densities at several wavelengths in the 575-nm band. All these ratios show the same behavior, corresponding to 575 nm. No trend toward a constant ratio was observed. At this time we do not know how this result can fit with the recently proposed model[10–12] in which these absorption bands are due to a single color center.

The study of the thermal stability of the γ-induced absorption bands has shown that all of the bands follow the same annealing kinetics. The results presented in Table I are quite different from those obtained by Barile,[6] probably because of the more detailed measurements made in this work. The existence of five annealing processes with the

TABLE I. Activation energy and pre-exponential factor of the five exponential annealing processes.

		Observed wavelength (nm)					
Expt.		576	395	336	227	195	T_M(°C)[a]
I	E(eV)	0.76 ± 0.03	0.76 ± 0.03	0.79 ± 0.07	0.72 ± 0.03	0.76 ± 0.02	194
	S(sec^{-1})	1×10^{6}	2×10^{6}	3×10^{6}	0.7×10^{6}	2×10^{6}	
II	E(eV)	1.02 ± 0.03	0.97 ± 0.04	1.02 ± 0.02	0.98 ± 0.04	1.05 ± 0.03	228
	S(sec^{-1})	2×10^{8}	0.6×10^{8}	2×10^{8}	0.9×10^{8}	5×10^{8}	
III	E(eV)	0.69 ± 0.01	0.72 ± 0.03	0.72 ± 0.04	0.68 ± 0.01	0.73 ± 0.01	240
	S(sec^{-1})	4×10^{4}	1×10^{5}	1×10^{5}	3×10^{4}	1×10^{5}	
IV	E(eV)	2.04 ± 0.05	2.11 ± 0.04	2.07 ± 0.06	2.25 ± 0.16	2.10 ± 0.09	313
	S(sec^{-1})	2×10^{16}	0.7×10^{17}	3×10^{16}	1×10^{18}	5×10^{16}	
V	E(eV)	0.75 ± 0.03	0.70 ± 0.05	0.72 ± 0.04	0.68 ± 0.04	0.72 ± 0.01	318
	S(sec^{-1})	1×10^{4}	5×10^{3}	1×10^{4}	3×10^{3}	0.8×10^{4}	

[a] Inflection points of the corresponding exponential decays, calculated from the experimental values of E_i and S_i, assuming a heating rate of 15 °C/min.

single-color-center models[9,10] indicates that this center plays the role of recombination center for mobile holes and/or interstitials which are liberated from five different traps. If the absorption bands are produced by several color centers, it would indicate that all these should have the same nature since they are annealed by the same complementary defect. The values of the pre-exponential factor expected in the case of mobile electrons or holes are in the range 10^7–10^{12}; only one of the values shown in Table I is in this range, so it is possible that mobile fluorine interstitials are involved in the annealing processes.

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