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Luminescence of F^+ centers in CaO crystals under pulsed-laser excitation

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Luminescence of F^+ centers (oxygen vacancies each with one electron) has been investigated in thermochemically reduced, electron-irradiated, and neutron-irradiated CaO crystals. Time-dependent emission spectra following laser excitation into the F^+ absorption band at 351 nm were measured for the three types of crystals. We observed a fast component with a lifetime ≤ 10 ns and a slow decay attributed to charge trapping and transport. The intensity and decay kinetics of the F^+ phosphorescence depended on the method by which the defects had been produced. Estimated gain coefficients for stimulated emission under pulsed laser pumping are less than 0.1 cm^{-1}. These values are significantly smaller than the absorption coefficient at the emission wavelength.

I. INTRODUCTION

Luminescence from oxygen-vacancy defects in calcium oxide has been the subject of several studies since the late 1960s.[1–4] Time-resolved luminescence of CaO under pulsed electron irradiation capable of displacement damage has been described.[5,6] There are two important reasons for extending the investigation of F^+ centers in CaO to include pulsed-laser excitation and associated time-resolved spectroscopy.

First, it has been reported that continuous-wave laser action was obtained in the blue region of the visible spectrum by using the F^+ center (an oxygen vacancy with one electron) in an electron-irradiated CaO crystal.[7] However, other researchers have been unable to achieve laser action with either continuous or pulsed pumping.[8–10] Failure to achieve laser action with pulsed laser pumping is particularly surprising in view of the higher achievable pump power density and the smaller number of absorbing metastable species in pulsed mode compared to cw operation. This difficulty in achieving laser action suggests rather complex behavior of the population dynamics and kinetics of F^+ centers in CaO under optical pumping conditions.

In the second place, this study of F^+ centers in CaO complements a recent time-resolved study[11] of F (an oxygen vacancy with two electrons) and F^+ centers in MgO using the same experimental techniques. The work on MgO showed that ionization of the defect excited state and recapture of the electron from shallow traps dominates the observed luminescence lifetime over at least nine decades from 20 ns out to tens of seconds, and is very nearly identical for both F and F^+ centers. This led to a fundamental conclusion about the location of the F^+ levels relative to the band edges, in reasonable agreement with recent theories.[12,13] It was also found that F^+ luminescence efficiency in MgO decreases significantly as pump power density is raised above 50 kW/cm^2. MgO and CaO are complementary subjects for spectroscopy because of their chemical and structural similarity on the one hand, coupled with an important contrast in relative peak position of F and F^+ absorption spectra in the two systems. The F and F^+ absorption bands overlap closely in MgO but are widely separated in CaO.

In general, the relative concentrations of F and F^+ defects and associated impurities in CaO crystals are dependent on the method used in the color-center production. In electron- and neutron-irradiated crystals, primarily F^+ centers are produced, with the concentration of F centers at least an order of magnitude smaller. Calcium oxide crystals that have been thermochemically reduced (TCR) during crystal growth normally have much higher concentrations of F centers. Since the absorption band of the F center is in the region of the F^+ emission, it is necessary that the concentration of F centers be small if the material is to exhibit optical gain. We have chosen to examine crystals that have been thermochemically reduced as well as those that have been electron- and neutron-irradiated in order to determine if the emission lifetime and spectroscopic properties of the F^+ center are dependent on the method used in the color-center production.

In this paper, we first survey the absorption and the emission properties of the color centers in our CaO crystals, using steady-state emission and excitation spectroscopy to identify the centers that are optically excited during pulsed excitation of the F^+ center. The technique of pulsed pumping and time-resolved spectroscopy is then used to observe the intrinsic F^+ fluorescence and the decay of the emission of other color centers, which are excited during optical excitation at 351 nm. In general, the F^+ emission will include the fluorescence of the F^+

center and phosphorescence due to ionization, trapping, and recombination effects. Our experiments provide an upper limit on the fluorescence lifetime of the F^+ center, from which an estimate of the gain coefficient can be made. The observation of long-lived phosphorescence indicates that the F^+ excited state ionizes, at least under pulsed laser excitation.

II. EXPERIMENTAL PROCEDURES

Single crystals of CaO were grown at the Oak Ridge National Laboratory using the arc-fusion method.[14] The selected crystals were clear and void-free. The crystals were cleaved to expose (100) faces and were 1–1.5 mm thick. Vacancies were produced by TCR during crystal growth[15] and via knock-on damage by energetic neutrons or electrons. Thermochemically reduced CaO crystals invariably contained significant amounts of hydrogen from OH contamination of the starting material, unless steps were taken to extract hydrogen either from the melt or from the finished crystal.[16] Thus we will refer to ordinary thermochemically reduced crystals as CaO:Ca:H, and those crystals in which protons have been extracted will be referred to as CaO:Ca. The hydrogen in the TCR crystals form a H^- ion, a proton in an oxygen vacancy site with two electrons, which is therefore positively charged with respect to the lattice. The charge state of the oxygen vacancy is primarily in the F state when H^- ions are present. When H^- ions are removed, F^+ centers become the predominant species. In the present study, a TCR crystal was heated to 1800 K in flowing nitrogen gas for 60 min to diminish the oxygen-vacancy concentration and to permit the protons to escape. The net result is that (1) the concentration of oxygen vacancies decreased approximately tenfold and (2) the absorption coefficient of the F^+ band became greater than that of the F band.

Although the irradiated crystals also contained hydrogen, it was not as significant for the F- and F^+-center spectroscopic properties for the following reason. During thermochemical reduction, the vacancies and the protons are mobile and can combine to form a substantial number of H^- centers. This clearly influences the equilibrium among F and F^+ centers, and furthermore H^- centers have been shown to be the dominant electron traps controlling F-center phosphorescence decay (in MgO), at least for times greater than seconds. On the other hand, the production of vacancy defects by oxygen displacement is not correlated significantly with hydrogen, and thus there is little opportunity for pairing of oxygen vacancies and hydrogen to form H^- centers. This is the basis for confining our emphasis on hydrogen to the thermochemically reduced crystals. Electron irradiation with a 1.8-MeV Van de Graaff accelerator was made to a dose of $\sim 5\times10^{18}$ electrons/cm^2 at about 340 K. The neutron irradiation was carried out to a dose of 2×10^{16} neutrons/cm^2 ($E>0.1$ MeV) at $\sim$320 K in the Oak Ridge Low Temperature Neutron Irradiation Facility.

A SPEX spectrofluorimeter capable of accepting a cryostat was used to measure the steady-state luminescence of the samples. For the time-resolved spectra, an optical multichannel analyzer (OMA) was employed. The system is an optoelectronic image device utilizing an array of photodiodes interfaced to a 10-ns gateable microchannel plate (MCP) image intensifier in the spectral image plane of a grating spectrometer. Gating of the MCP (or for times longer than $\sim$3 ms, opening of a shutter) occurred at a preset delay after the laser pulse to provide time resolution from 10 ns to 100 s.

Alternatively, to measure the decay time of the F^+ luminescence at specific wavelengths, the CaO sample was excited with a short pulse of 351-nm light, and the luminescence was passed through a monochromator onto an RCA 8575 photomultiplier tube (PMT). The electronic signal generated in the PMT was digitized in sequential 10-ns intervals and stored. To display decay curves spanning up to eight decades, segments covering about two decades each were sequentially normalized so as to fit smoothly together in overlapping regions.

The ultraviolet laser source that irradiated the samples was a XeF excimer laser having an output pulse of 10-ns width [full width at half maximum (FWHM)] and an energy output of 130 mJ/pulse at 351 nm. The laser energy density on the sample in these experiments was 0.75 J/cm^2.

III. RESULTS AND DISCUSSION

A. Absorption and steady-state luminescence of defects in CaO

Figure 1 shows the absorption spectra of F^+ and F centers at 340 and 400 nm, respectively, in CaO:Ca, in

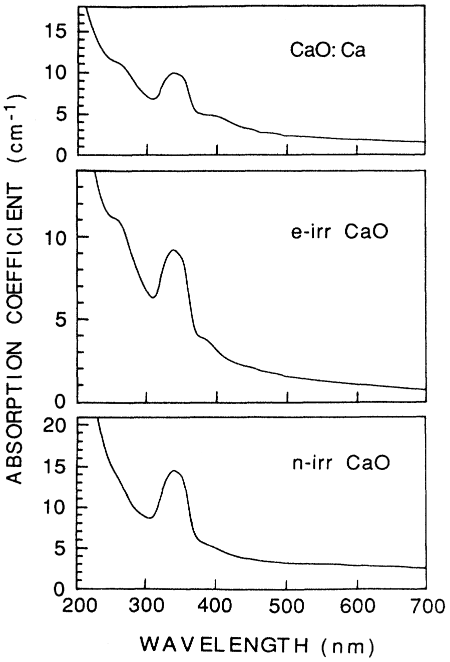

FIG. 1. Optical-absorption spectra of CaO:Ca, 5×10^{18} e/cm^2 electron-irradiated (e-irr) and 2×10^{16} n/cm^2 neutron-irradiated (n-irr) CaO crystals, measured at room temperature.

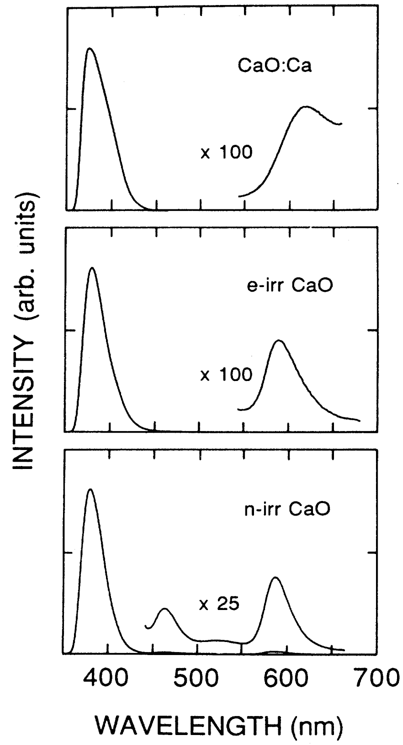

FIG. 2. Emission spectra from 340-nm (F^+ center) excitation of CaO:Ca, 5×10^{18} e/cm^2 electron-irradiated and 2×10^{16} n/cm^2 neutron-irradiated CaO crystals, measured at room temperature.

electron-irradiated, and in neutron-irradiated CaO crystals. The emission spectra from excitation of F^+ centers at 340 nm in each crystal are shown in Fig. 2. The band at 620 nm in the CaO:Ca crystal is due to F-center emission and the bands at 585 nm in the irradiated crystals are attributed to emission from F-aggregate centers. Other centers produced by thermochemical reduction, electron irradiation, and neutron irradiation in CaO crystals have characteristic emission bands. Table I lists the excitation and emission bands that we observed in the three types of crystals at room temperature. All three crystals exhibited emission bands at 370, 463, and 530 nm and corresponding excitation bands at 345, 267, and 430 nm, respectively. Several authors have studied in detail the 370-nm band of F^+-center emission ($^2T_{1u}\rightarrow{}^2A_{1g}$) upon excitation of a CaO crystal in the F^+ absorption band at 354 nm.[17,18] At low temperatures a zero-phonon line is observed at 355.7 nm in both absorption and emission.

The broad band that we observed at 463 nm in all the crystals under uv excitation appears to be the same as the so-called deformation-induced emission band.[19] Chen *et al.*[19] studied the luminescence spectra of deformed crystals in the alkaline-earth oxides under excitation with uv light. They reported a deformation-induced luminescence band at 2.6 eV with a FWHM of 0.65 eV. The excitation spectrum for the weak emission band at 530 nm peaked at 430 nm. These emission and excitation bands may involve transition-metal impurities.

From the data in Table I one can anticipate which emission bands are likely to appear in the time-resolved spectra following pulsed-laser excitation at 351 nm. It is

TABLE I. Excitation and emission bands from CaO:Ca, electron-irradiated CaO with a dose of 5×10^{18} e/cm^2, and neutron-irradiated CaO with a dose of 2×10^{16} n/cm^2. Note: There exist two emission bands at 463 nm. In one case, the absorption or excitation band occurs at 267 nm; these are due to "deformation" bands (Ref. 19). In the second case, the emission at 463* nm results from the excitation band at 310* nm. The corresponding bands are marked with an asterisk. The 410-nm band in electron-irradiated crystals was deduced by comparing the F^+ band with that in a neutron-irradiated crystal.

	Excitation band (nm)	Emission band (nm)
CaO:Ca	267	463 (deformation band)
	345(F^+)	370(F^+)
	400(F)	620(F)
	430	530
Electron-irradiated CaO	267	463 (deformation band)
	345(F^+)	370(F^+)
	430	530
	310*	463*
	355,570(F_2)	585(F_2)
		410
Neutron-irradiated CaO	267	463 (deformation band)
	345(F^+)	370(F^+)
	430	530
	310*	463*
	355,570(F_2)	585(F_2) (Refs. 20 and 21)

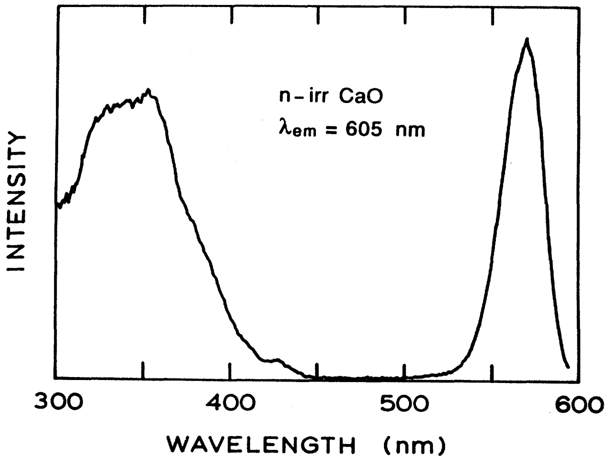

FIG. 3. Excitation spectrum for the 585-nm emission band detected at 605 nm in a neutron-irradiated CaO crystal at room temperature. The intensity is in arbitrary units.

evident that the F^+ center should be excited in all three types of crystals. In addition, the irradiated crystals exhibit an emission band at 585 nm. The 585-nm emission band has been identified as an F-aggregate or F_2-type center.[20,21] This band was much more prominent in the neutron-irradiated crystals than in those irradiated by electrons. The room-temperature excitation spectrum for the 585-nm emission band detected at 605 nm is shown in Fig. 3. The excitation band at 570 nm corresponds to transitions from the ground state to the lowest excited state of the F_2-type center. There is a relatively small Stokes shift between the excitation and emission bands. The excitation spectrum shows that the F_2-aggregate center also has excitation bands corresponding to higher excited states, which strongly overlap the absorption bands of the F^+ center. Not evident from the data in Table I is that excitation at 353 nm of the CaO:Ca crystal also resulted in F emission at 620 nm, because the F^+ emission overlaps the F absorption, as noted earlier. Figure 4 illustrates steady-state emission spectra from 450 to 700 nm for the CaO:Ca and neutron-irradiated crystals with 353-nm excitation. In this range the irradiated crystal showed only the narrow emission band from the F_2-type center, whereas the CaO:Ca crystal exhibited only the much broader emission at 620 nm from F centers. The emission from the electron-irradiated crystal in this spectral region was negligible.

B. Time-resolved luminescence spectra under pulsed excitation

Figures 5–7 are pseudo-three-dimensional presentations of luminescence spectra versus time following 351-nm laser excitation of the F^+ absorption band in thermochemically reduced, electron-irradiated, and neutron-irradiated CaO crystals. The 351-nm excitation wavelength falls within the F^+ absorption band in CaO. Peak power density of the excitation was about 75 MW/cm^2. All spectra recorded at successive times after the pulse for a given crystal have been normalized to constant slit width and exposure time relative to the earliest recorded spectrum. The emission from CaO:Ca (Fig. 5) is almost entirely that of the F^+ center. The time-resolved spectra of the neutron-irradiated crystal (Fig. 7) shows the emission from the F^+ center along with a 585-nm emission band from the F_2-type center. An additional emission band near 460 nm, which is not identified, also appears in the neutron-irradiated crystals. Finally, the time-resolved spectra of the electron-irradiated crystal in Fig. 6 shows the predominant emission is that of the F^+ center. However, the shape of the emission band changes as a function of time, with the low-energy tail becoming more pronounced for later times. This is due to the pres-

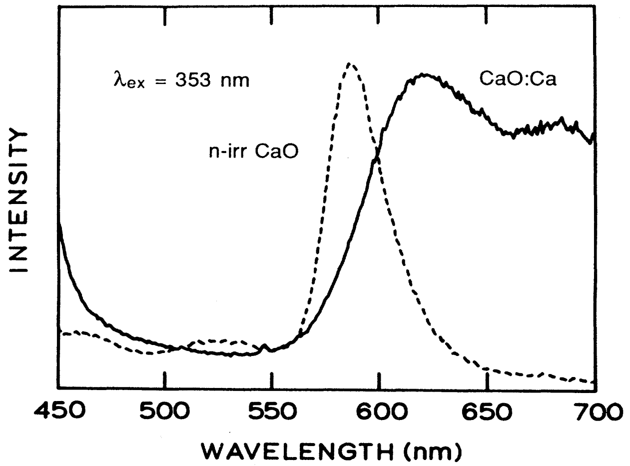

FIG. 4. Emission spectra of 585- and 620-nm bands excited at 353 nm from a CaO:Ca crystal and a neutron-irradiated CaO crystal at room temperature. The intensity is in arbitrary units.

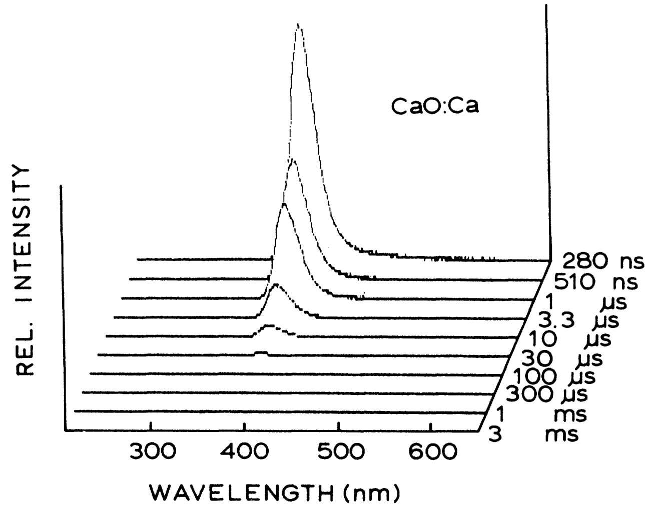

FIG. 5. Luminescence spectra vs time following 351-nm excitation by XeF excimer laser pulses in CaO:Ca crystal at room temperature.

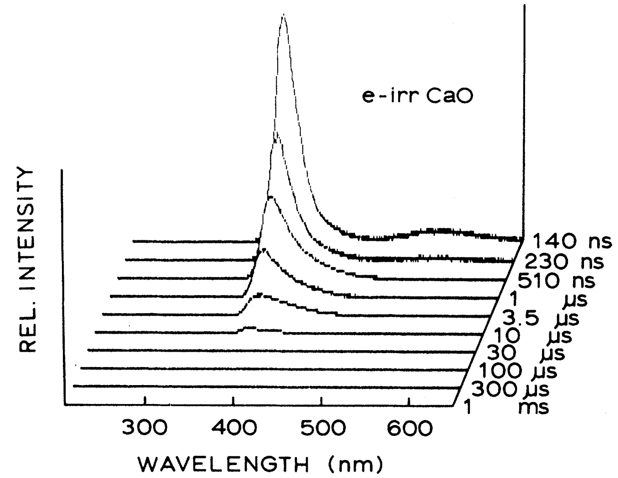

FIG. 6. Luminescence spectra vs time following 351-nm excitation by XeF excimer laser pulses in a 5×10^{18} e/cm^2 electron-irradiated CaO crystal at room temperature.

ence of an underlying emission band at 410 nm, which we have observed only in the electron-irradiated crystals. The somewhat slower time decay of the 410-nm emission band accounts for the exaggeration of the low-energy side of the F^+-center emission band as time progresses.

C. Decay time of F^+ luminescence in CaO

In this subsection we examine the decay of luminescence of F^+ centers in CaO at the fixed wavelength of 415 nm following laser excitation at 351 nm. The greater sensitivity of our instrumentation for time-decay measurements at a single wavelength allows us to follow the luminescence over nine decades, from 20 ns up to 50 s.

The luminescence decay curves following 10-ns pulsed excitation of F^+ centers in TCR, electron-irradiated, and neutron-irradiated CaO crystals are shown in Figs. 8–10, at temperatures of 77 and 295 K. The experimental results do not show simple exponential decay curves of the luminescence. The long persistence of the decay is strongly suggestive of radiative recombination with carriers thermally released from traps just as in MgO.[11]

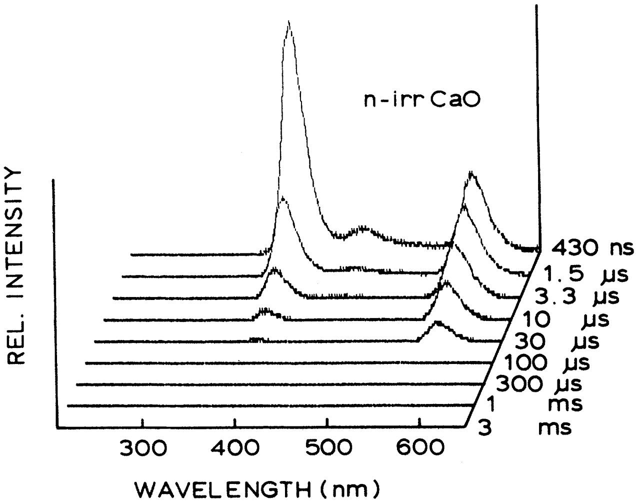

FIG. 7. Luminescence spectra vs time following 351-nm excitation by XeF excimer laser pulses in a 2×10^{16} n/cm^2 neutron-irradiated CaO crystal at room temperature.

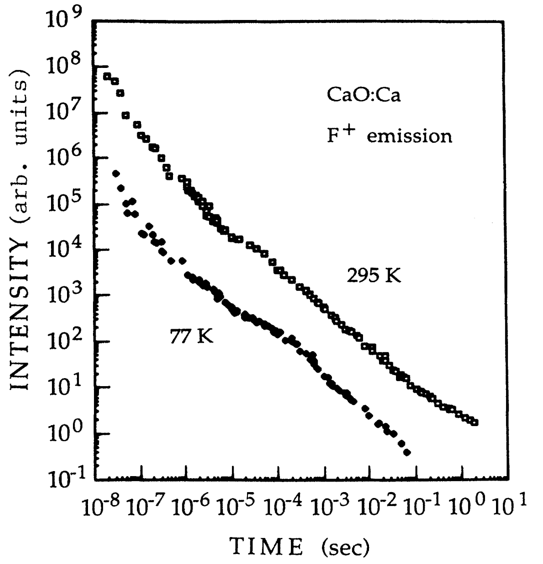

FIG. 8. Fluorescence decay curves at 295 and 77 K, following 351-nm excitation of the F^+ centers in a CaO:Ca crystal. The emission was monitored at 415 nm. The relative intensities at 295 and 77 K were not determined.

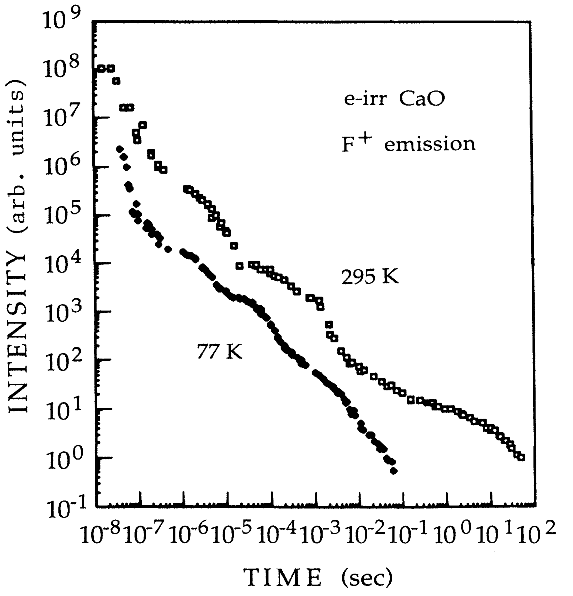

FIG. 9. Fluorescence decay curves at 295 and 77 K, following 351-nm excitation of the F^+ centers in an electron-irradiated CaO crystal (dose $=5\times10^{18}$ e/cm^2). The emission was monitored at 415 nm. The relative intensities at 295 and 77 K were not determined.

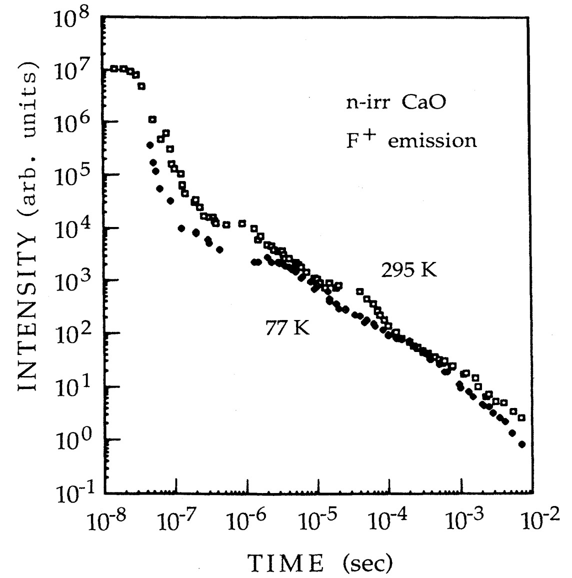

FIG. 10. Fluorescence decay curves at 295 and 77 K, following 351-nm excitation of the F^+ centers in a neutron-irradiated CaO crystal (dose$=2\times10^{16}$ n/cm^2). The emission was monitored at 415 nm. The relative intensities at 295 and 77 K were not determined.

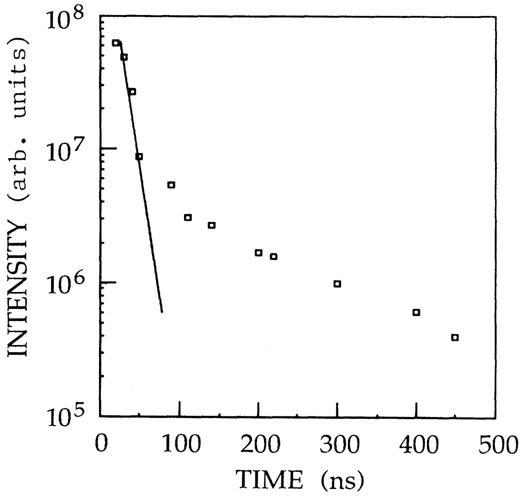

FIG. 11. Fluorescence lifetime of the F^+ center was shown to be ~10 ns for a CaO:Ca crystal using the slope from the initial part of decay curve. Intensity is an arbitrary unit.

There are slight variations in the details of the phosphorescence in the three types of crystals. However, we believe that this variation is due to the different types of traps inherent in the methods of defect production. The long decay time of the F^+ luminescence is not much different at 77 and 295 K, as shown in the figures. In all three types of CaO crystals, room-temperature measurements show that the fast component ($t < 50$ ns) comprises only about 7% of the time-integrated F^+ luminescence, with the remaining 93% attributed to the slow decay behavior. Low-temperature measurements at 77 K show that slightly more of the integrated luminescence, 9%, is contributed by the fast intrinsic decay. The decay curves for all three crystals are dominated by the long-term phosphorescence, indicating that the F^+ center is not optically stable following 351-nm laser excitation. In this respect, the time decay of the F^+ luminescence in CaO behaves like that in MgO.[11]

An estimate of the fluorescence lifetime of the F^+ center can be obtained by plotting the initial luminescence decay in CaO:Ca on a semilogarithmic plot as shown in Fig. 11. We obtain a fluorescence lifetime of ≤ 10 ns, the time-resolution limit of our instrumentation. The ${}^2T_{1u}\rightarrow{}^2A_{1g}$ transition responsible for the F^+ luminescence should be strongly allowed. We suggest that 10 ns is the intrinsic lifetime, i.e., the radiative lifetime of those F^+ centers that do not ionize in the excited state. The long decay evident in Figs. 8–10 can be explained by virtue of ionization from the F^+ excited state, charge trapping, and subsequent recombination to yield the F^+ phosphorescence.

The similarity of the F^+ luminescence decay curves at both 77 and 295 K implies either that the traps involved are very shallow, or that the recombination proceeds primarily by tunneling as in donor-acceptor pair luminescence.[22] Even though the H^- concentration is low, they are nevertheless important electron traps. The H^- ions were found to be important contributors to the long lifetime of both F luminescence[23] and F^+ luminescence[11] in MgO. There is indication now that reducing the H^- concentration in CaO reduces the F luminescence lifetime and the F/F^+ ratio in steady state.[4] The effect of H^- ions on F^+ luminescence lifetime in CaO is not known yet.

Since laser action has been reported from F^+ centers in CaO, it is of interest to estimate the cross section and gain coefficient using our data on the decay time of F^+ luminescence. If charge trapping and transport are the cause of the long F^+ luminescence decay time we have observed, the fraction of excited F^+ centers associated with the slow decay, e.g., 93%, cannot contribute to stimulated emission during pulsed pumping. That is, while the trapped carrier is resident on a site physically removed from the recombination center (F^+ center), that center cannot contribute to stimulated emission. The effective stimulated-emission cross section per excited center under pulsed excitation conditions will be reduced in proportion to the fraction of the time-integrated luminescence, which has the intrinsic (≤ 10 ns) lifetime. We have determined this fraction to be 7–9 % for the crystals studied. This deficiency may not be so serious under continuous pumping, provided the luminescence quantum yield is constant with increasing pump power. However, this characteristic domination of the lifetime by charge trapping provides an important reason for the failure to achieve laser action under pulsed pumping.

For a four-level system, with a Gaussian emission band centered at λ_0 (μm), and the FWHM represented as $d\nu$ (Hz), the gain coefficient α_0 (cm^{-1}) at the band peak can

TABLE II. Estimated parameters yielding gain coefficients for the F^+ centers in CaO:Ca, electron-irradiated, and neutron-irradiated CaO crystals. The derived gain coefficient is based on a quantum efficiency of unity, which is considered a highly optimistic value. ( )* values were not quoted by the authors, but were deduced from $N^*(F^+)$ and $\alpha_{0_{\max}}$ (cm^{-1}).

Samples	$N^*(F^+)$ (cm^{-3})	t (ns)	$\sigma_{\max}$ (cm^2)	$\alpha_{0_{\max}}$ (cm^{-1})
CaO:Ca	4.2×10^{15}	10	3.1×10^{-18}	0.013
Electron-irradiated CaO	6.2×10^{15}	8	3.7×10^{-18}	0.023
Neutron-irradiated CaO	6.9×10^{15}	8	3.7×10^{-18}	0.026
Henderson (Ref. 7)	$\sim1\times10^{16}$	5	$(1.9\times10^{-16})^*$	1.9
Duran (Ref. 25)	5×10^{17}		$(5.8\times10^{-18})^*$	2.9

be calculated from[24]

$$\alpha_0=\sigma N^*=\frac{N^*\lambda_0^2\eta}{8\pi n^2\tau}\,\frac{1}{1.07\delta\nu}\,, \tag{1}$$

where σ is the effective transition cross section, N^* is the excited-state population, η is the quantum efficiency, n is the refractive index, and τ is the radiative decay time. Table II shows the values for the F^+ center in the three types of CaO crystals.

Assuming (1) an optimistic quantum efficiency of 1, (2) $N^*\approx N/2$, and (3) the entire decay proceeds with the 8–10-ns intrinsic lifetime, we find upper limits on the stimulated emission cross section and gain coefficient, $\sigma_{\max}$ and $\alpha_{\max}$, as listed in Table II. The cross sections are all about 10^{-18} cm^2. The gain coefficients in all three crystals are all less than 0.1 cm^{-1}. These are smaller than the gain coefficients estimated by Henderson[7] and by Duran.[25] The input parameters assumed or measured for each of the three estimates are listed in Table II. As noted earlier, the attainable values of optical gain under pulsed pumping in these crystals should be only 7–9 % of the listed values because most of the excited population is locked up in the charge-trapping sites. Therefore the upper limit of the gain coefficient is <0.01 cm^{-1}. Furthermore, there are appreciable losses due to absorption in the region of the F^+ center emission that must be overcome to achieve lasing. The losses stem primarily from the absorption of the F center at 400 nm. In a typical neutron-irradiated crystal, the absorption coefficient at 400 nm due to the presence of F centers is on the order of 1 cm^{-1}. This value does not include the transient losses that might occur during laser pumping. Recent photoconversion experiments show that excitation of the F^+ center results in an increase in the number of F centers in the crystal that persists for times greater than 10^3 s.[4,26] In some cases, the absorption coefficient at 400 nm increases by a factor of 2. If the intensity of the phosphorescence observed after laser excitation is correlated with the number of populated traps in the crystal, then the losses due to transient color centers likely exceed those in steady state by a substantial factor.

IV. SUMMARY

We have investigated the time-dependent emission of the F^+ center in CaO for electron- and neutron-irradiated and thermochemically reduced crystals. Laser excitation at 351 nm produces primarily emission from the F^+ center for all three types of crystals. For the neutron-irradiated crystals, there is an additional emission band at 585 nm corresponding to fluorescence from an F_2-type center. One of our most important findings is that the time dependence of the F^+-center luminescence is dominated by slow phosphorescence, presumed to result from the recombination of trapped electrons with ionized F^+ centers. The ratio of intrinsic fluorescence to phosphorescence was not significantly altered by temperature. The large number of charge carriers released following the optical excitation demonstrates that the F^+ center is unstable during optical pumping. Estimated maximum gain coefficients in all cases were less than 0.1. In addition, identification of charge-trapping control of the F^+ luminescence lifetime suggests that the effective maximum gain coefficient for pulsed pumping will be only 7–9 % of this value. This is to be compared to the absorption coefficient of F centers at 400 nm, which was greater than 1 cm^{-1} in all three types of crystals. In view of this, we conclude that CaO crystals must possess much lower background absorption and either much less excited-state ionization or shorter trap-dominated recombination times if an F^+ laser is to be achieved. To our knowledge, such crystals do not exist. It is indeed likely that such desirable properties are not characteristic of the intrinsic F^+ center. We propose that these properties may be more compatible with the F^+ center perturbed by an aliovalent impurity.

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