

F BAND IN X- AND ELECTRON-IRRADIATED CaF₂

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This Letter reports an investigation using pulsed electron irradiation to determine if the low efficiency of *F*-band coloration in calcium fluoride is caused by the instability of the *F* center. No transient *F* centers were seen in times as short as 2×10^{-7} sec. It is concluded that the inherent efficiency of *F*-band coloration in CaF₂ is small compared with similar processes in alkali halides and a possible reason for this is discussed.

Calcium fluoride has been extensively studied and is found to be more difficult to color than alkali halides and to have absorption spectra which vary widely¹ with coloration method, crystal origin, and impurity content.

Two intrinsic color centers have been observed in CaF₂ by electron spin-resonance techniques. One is the V_K , or self-trapped hole, whose resonance has been reported by Hayes and Twidell² in x-rayed CaF₂ at liquid-nitrogen temperatures (LNT). The other is the *F* center, an electron trapped in an anion vacancy, whose resonance has been found by Arends³ in additively colored crystals and correlated with an optical absorption band at 375 nm.⁴

In general, the literature indicates that the *F* band in CaF₂ can be created at room temperature (RT) only by additive coloration. It has been observed at liquid-helium temperatures (LHeT) after electron irradiation by Kamikawa *et al.*⁵ but they reported it could not be produced at LNT. Ratnam⁶ has reported its production by x rays in rather complex spectra but only between 180 and 250°C. But an *F* band produced by ionizing radiation at RT has not been reported.

In the present work, a specially prepared "rare-earth free" crystal from Harshaw Chemical Company has been used. Emission spectroscopic analysis showed manganese (10-100 ppm) as the principal impurity and no detectable rare earths.

Typical experimental results are shown in Fig. 1. Curve 1 shows the absorption produced by 2.0-MeV electrons (1.5 μ A for 20 min) at LNT. The change in absorption resulting from bleaching optically with 450-nm light or thermally by warming to RT in the dark is shown

by the dashed curve 2. This curve shows that three bands have been bleached whose maxima are at 229, 320, and 450 nm. Curve 2 also represents the spectrum produced by 50-kV x rays at LNT; that is, the same three bands are produced at LNT by both electron and x-ray irradiations. Irradiation at LHeT gives essentially the same result.

Warming to RT in the dark bleaches all three bands leaving a small band peaked at 380 nm. Recooling the crystal to LNT gives curve 3 in which it is apparent that some additional absorption remains on the long-wavelength side of the 380-nm band. This may account for its displacement from Arends' peak position at 375 nm. Positive identification by ESR was not possible due to the strong masking resonance of Mn²⁺ but the similarity of peak position and half-width with previous data^{3,5} make plausible the identification of this absorption as the *F* band, shifted slightly and perhaps impurity stabilized in some yet unknown manner. The RT band produced by a 70-min x irradiation at RT is shown by curve 4. The band is still quite small, however, with the peak

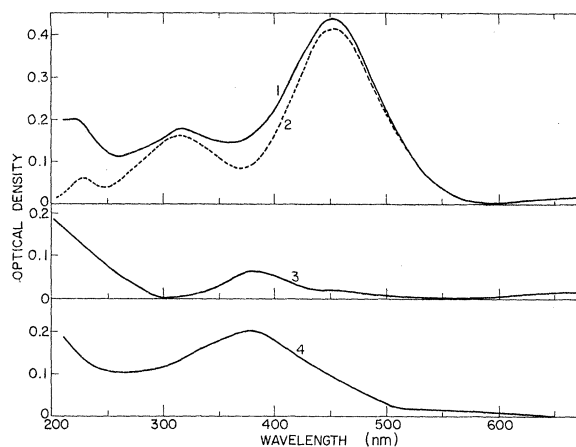


FIG. 1. Absorption of rare-earth-free CaF₂:Mn single crystal. Curve 1: At LNT after 2.0-MeV electron irradiation (20 min, 1.5 μ A) at LNT. Curve 2: Lost by bleaching with 450-nm light at LNT or warming to RT. Curve 3: At LNT after warming to RT. Curve 4: At RT after extended RT x irradiation (50 kV, 30 mA, 70 min).

optical density of 0.2 corresponding to an absorption coefficient of less than 2 cm^{-1} .

To examine the possibility that more F centers are instantaneously created but disappear before measurement, we have measured the transient absorption spectrum of this crystal at RT using 0.4- μsec pulses of 15-MeV electrons from the Naval Research Laboratory Linac facility. Immediately after the electron pulse, the three-band spectrum characteristic of low-temperature irradiation (curve 1) is observed. This spectrum quickly decays away leaving the stable F band. The decay lifetimes of the three bands are 20 μsec for the 229-nm band, 30 μsec for the 320-nm band, and 20 μsec for the 450-nm band.

A careful investigation of the 300- to 450-nm region failed to show any variation from this result! That is, although transient three-band spectra comparable in size to those resulting from extended low-temperature irradiations were produced, no evidence of a transient F band was found at times longer than 0.2 μsec . Thus, it is concluded that the difficulty of producing F centers in CaF_2 by ionizing radiation is due to a low production efficiency rather than to production of unstable F centers which rapidly decay.

This result may be understandable in terms of the focused collision mechanism for production of separated interstitials and vacancies initially suggested by Silsbee.⁷ In this model, irradiation produces an initially displaced halogen ion which strikes one of its neighbors and starts a "billiard ball" process of sequential atomic displacements. Computer simulations of three-dimensional ionic motion by Torrens and Chadderton⁸ for face-centered cubic alkali halides have shown that focusing can occur in several low-index directions, particularly in $\langle 110 \rangle$ directions. The $\langle 110 \rangle$ focusing is assisted by ionic "lenses" which are sym-

metrically arranged about that direction. The process propagates a dynamic crowdion along the preferred direction until an interstitial halide ion is finally produced many lattice distances from the starting-point vacancy. The vacancy can then trap an electron to become an F center.

In CaF_2 , however, the calcium ion is doubly charged and preservation of charge neutrality requires that every other site in the positive-ion sublattice be empty. In this case, the positive ions are no longer symmetrically arranged about any simple anion row and the ionic "lenses" are considerably altered. Thus it seems likely that focusing in any single direction may not occur in this situation and that the "billiard ball" sequence will be deflected by the empty lattice sites. This would leave the resulting interstitial much closer to its partner vacancy and more likely to recombine with it with a consequent decrease in the efficiency of F -center formation by this mechanism.

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