

## Color Center Production in $\text{CaF}_2\text{Sm}^{3+}(\text{Y}^{3+})$ by Ultraviolet Irradiation

T. EWANIZKY

*U. S. Army Electronics Laboratories, Fort Monmouth, New Jersey*

(Received 30 January 1964)

Color centers have been produced in certain  $\text{CaF}_2\text{Sm}^{3+}$  crystals by ultraviolet irradiation. The color centers are attributed to reduction of  $\text{Y}^{3+}$  impurities. Although no  $\text{Sm}^{3+}$  reduction was observed, its presence was found to be indispensable for ultraviolet coloration. A complex is proposed, within which charge transfer takes place.

### INTRODUCTION

DURING an investigation of  $\text{CaF}_2\text{Sm}^{3+}$ , it was discovered that certain crystals were colored a deep blue by 2537-Å Hg lamp irradiation. Absorption curves made of a colorable specimen revealed an ultraviolet edge, seen in Fig. 1, to begin at  $\sim 2700$  Å. Irradiation into this edge, or at shorter wavelengths, rapidly produced coloration. The color center is identified as  $\text{Y}^{2+}$ .<sup>1</sup>  $\text{Y}^{3+}$  is a common impurity in fluorite starting materials.

$\text{Y}^{3+}$  and  $\text{Sm}^{3+}$  in  $\text{CaF}_2$ , were both recently reported to be reduced by irradiation. In all cases, however, the irradiation was by x rays, gamma rays, or high-energy particles.

In some of the crystals investigated here, the effects observed seem to contradict the referenced literature.

(1) In Ref. 1,  $\text{Y}^{3+}$  reduction was reported to be completely suppressed by small quantities of  $\text{Sm}^{3+}$ . In our crystals, however, even though no direct participation of  $\text{Sm}^{3+}$  in the coloring process was noted, its presence was indispensable for reduction of the  $\text{Y}^{3+}$ .

(2) High-energy irradiation was found<sup>2</sup> to be effective in the reduction of  $\text{Sm}^{3+}$  in  $\text{CaF}_2$ . In fact, this technique has become a common method for production of certain divalent ions, in crystals which cannot ordinarily be grown from the melt.

On the contrary, no significant  $\text{Sm}^{3+}$  reduction was observed in our crystals, although  $\text{Y}^{3+}$  reduction was easily accomplished by appropriate uv irradiation. A crystal was exposed to 1.5-MeV electrons and although the  $\text{Y}^{2+}$  color centers were rapidly formed, no significant  $\text{Sm}^{3+}$  reduction was observed even after considerable dosage.

It is proposed that the particular charge compensation of the impurities is of primary significance in the charge transfer and reduction processes.

### EXPERIMENTAL PROCEDURE

The absorption curves in Fig. 1 describe one of these crystals in various stages of coloration. They were made with a Cary 14 recording spectrophotometer. It is obvious that each spectrum is a composite due to a

number of contributing impurity ions. In the figure, curve A depicts the crystal in its normal, unirradiated condition. Readily visible are some absorption bands and lines due to different ions and they are identified as follows:

In Fig. 1(a) (77°K) curve A:

(1) The bands at  $\sim 4200$  and  $6300$  Å and the sharp line at  $6900$  Å are due to the divalent samarium ion.<sup>3</sup>

(2) The sharp lines at  $\sim 4000$  Å are due to the trivalent samarium ion.

(3) A broad line at  $\sim 2550$  Å believed to be due to  $\text{Sm}^{3+}$  ion-pair resonance absorption.<sup>4,5</sup>

(4) A very intense, rather steep, absorption edge from  $\sim 2700$  Å to shorter wavelengths. This absorption edge rises to at least an order of magnitude higher than the maxima and persists to both the optical density and short wavelength limit ( $1850$  Å) of the instrument.

In Fig. 1(b) (300°K), the bands are thermally broadened due to lattice interaction. No large broadening of the  $\text{Sm}^{3+}$  lines at  $\sim 4000$  Å occurs since they are associated with shielded  $4f-4f$  transitions, common in the trivalent rare earths.

### COLORATION

The crystal was irradiated by uv light derived from a 1000-W xenon lamp through a monochromator with 200-Å bandwidth. Periods of irradiation were generally less than one-half hour. Longer irradiation times would produce a dark blue coloration and absorption bands formed would surpass the limit of ability for direct measurement by the spectrophotometer. No measurements of crystal coloration versus irradiation time were made.

Coloration could be accomplished only when the monochromator was adjusted to emit wavelengths corresponding to the uv absorption edge or shorter wavelengths.

The charge transfer process is dependent on the temperature of the crystal during irradiation.

If the crystal is irradiated while in a liquid-nitrogen bath, no apparent reduction or coloring is observed. An absorption curve taken at this time, however, shows

<sup>3</sup> W. Kaiser, C. G. B. Garrett, and D. L. Wood, *Phys. Rev.* **123**, 766 (1961).

<sup>4</sup> F. Varsanyi and G. H. Dieke, *Phys. Rev. Letters* **7**, 442 (1961).

<sup>5</sup> G. H. Dieke and E. Dorman, *Phys. Rev. Letters* **11**, 17 (1963).

<sup>1</sup> J. R. O'Connor and J. H. Chen, *Phys. Rev.* **130**, 1790 (1963).

<sup>2</sup> J. R. O'Connor and H. A. Bostick, *J. Appl. Phys.* **33**, 1868 (1962).

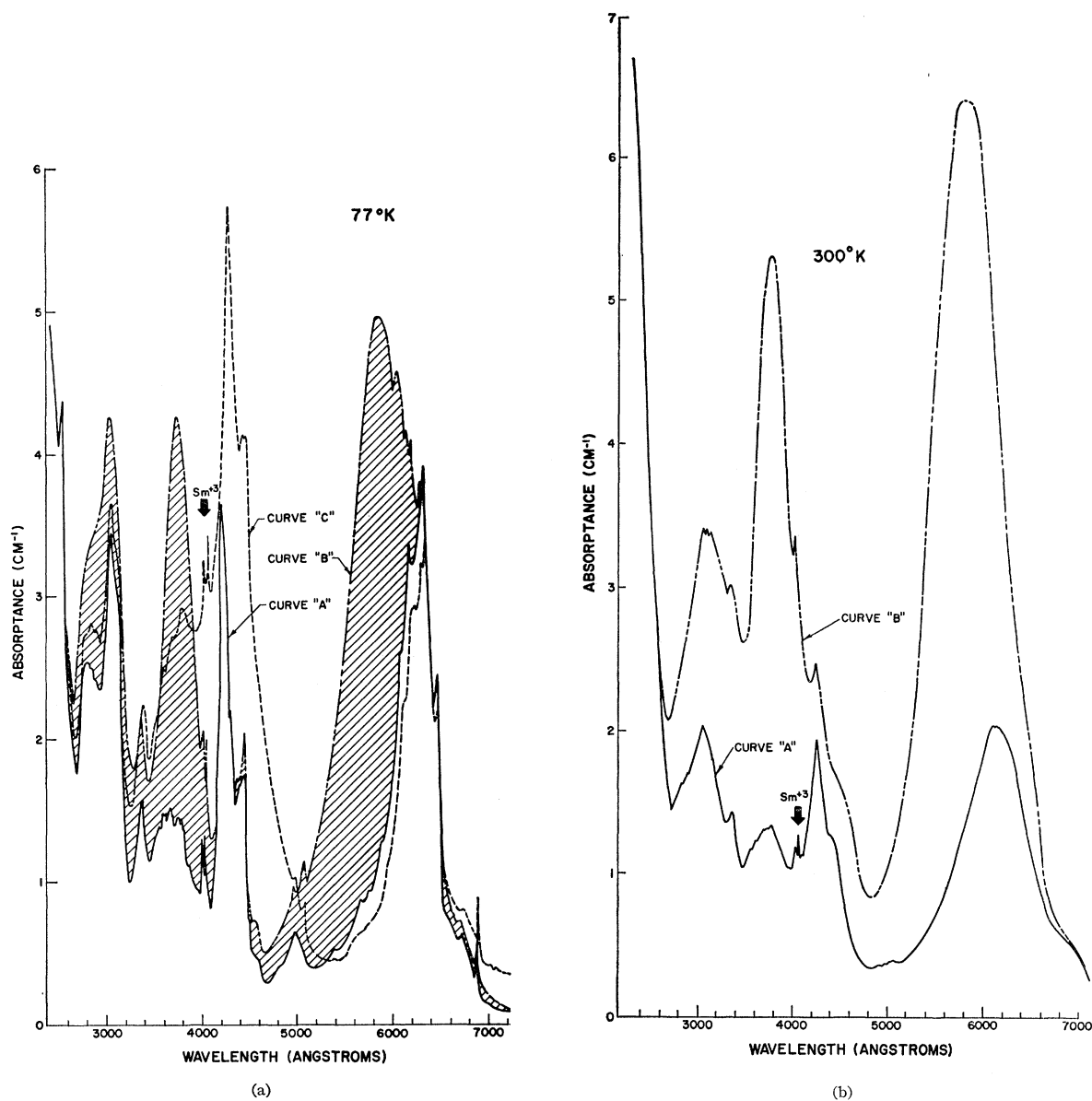


FIG. 1. (a) and (b). Absorbance at 77 and 300°K of a  $[\text{CaF}_2:\text{Sm}^{3+}(\text{Y}^{3+})]$  crystal in various stages of coloration. In both figures, curve A represents normal absorbance and curve B is absorbance after coloration. Curve C is discussed in the text.

that the original spectrum is substantially changed. A broad underlying band at  $\sim 3900 \text{ \AA}$  and a low tail from  $\sim 6500$  to  $8500 \text{ \AA}$  emerges [see Fig. 1(a), curve C]. This particular spectrum is stable as long as the crystal is maintained at 77°K after irradiation. If the crystal is lifted from the bath, gradual blue coloration appears as it warms to room temperature. Upon returning the crystal to liquid-nitrogen temperature, the absorption spectrum of Fig. 1(a), curve B results. If the irradiation is applied with the crystal at room temperature, the transfer occurs immediately and coloration appears rapidly.

Both processes yield identical coloration and three prominent new bands appear at  $\sim 3000$ ,  $3800$ , and

$5800 \text{ \AA}$ . These bands are identified as three components of the  $\text{Y}^{2+}$  spectrum.<sup>1</sup> The fourth component, which would be expected at  $\sim 2250 \text{ \AA}$ , is lost in the uv absorption edge.

#### BLEACHING

Heat or infrared irradiation produced rapid bleaching of the crystal and returned it to its original condition. This is similar to the bleaching effect reported by O'Connor and Chen.<sup>1</sup>

#### DISCUSSION

A search was made of available  $\text{CaF}_2:\text{Sm}$  crystals. They had various shades of normal coloration, from

water clear to a dark green. The Sm and Y concentrations, in the crystals, were approximately of the same order of magnitude. The Sm content was, typically, 0.001 to 0.005 mole percent. From this preliminary investigation, it was found that the only colorable specimens were those which exhibited a "Type I"  $\text{CaF}_2:\text{Sm}^{3+}$  fluorescence spectrum.<sup>6</sup> Absorption curves made of these crystals showed more or less evidence of the  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  lines and bands as in Fig. 1. Significantly, however, the steep uv absorption edge was present in all. In light green crystals (some  $\text{Sm}^{2+}$  content) the edge started at  $\sim 2700 \text{ \AA}$ . In clear crystals (virtually no  $\text{Sm}^{2+}$  content, which is indicative of oxygen contamination<sup>7</sup>) the edge receded  $\sim 200 \text{ \AA}$  toward shorter wavelengths.

Since coloration did not alter the character or intensity of the  $\text{Sm}^{2+}$  spectra, this ion is not believed to be an active agent in the charge transfer processes.

The coloration and bleaching is remarkably efficient and rapid and may be easily accomplished with relatively low irradiation energies. Also, although the  $\text{Sm}^{3+}$  ions are not visibly affected during the processes, their presence is indispensable for uv induced  $\text{Y}^{3+}$  reduction. These observations tend to suggest the existence of a complex, within which charge transfer may occur. In order to correlate observation with hypothesis, the necessary elements in the complex would be  $\text{Sm}^{3+}$ ,  $\text{Y}^{3+}$ , and a third component which is ionized by uv irradiation.

$\text{Y}^{3+}$  impurities in  $\text{CaF}_2$  are known to be closely

<sup>6</sup> I. V. Stepanov and P. P. Feofilov, Dokl. Akad. Nauk (SSSR) **108**, 165 (1956) [English transl.: Soviet Phys.—Doklady **1**, 350 (1957)].

<sup>7</sup> H. Guggenheim, J. Appl. Phys. **32**, 1337 (1961).

associated with  $\text{F}^-$  interstitials.<sup>8</sup> Presumably, the trivalent ion is charge compensated by an  $\text{F}^-$  interstitial in a neighboring position. Perhaps the effect of the  $\text{Sm}^{3+}$  in the complex is to weaken the bonding between the interstitial fluorine atom and its captured electron. The perturbed interstitial may then be sensitive to uv irradiation. The energy necessary for dissociation of the bound electron may be represented by the uv absorption edge, which has the appearance and character of an ionization continuum. Oxygen must also be an influential factor since its presence (in the clear crystals) shifts the edge over a considerable distance.

No explanation can be given for the anomalous spectrum produced [Fig. 1(a), curve C] when the crystal is irradiated and maintained at  $77^\circ\text{K}$ . The fact that thermal energy is able to release the electron indicates the existence of a shallow trap. However, it is difficult to explain how such a shallow trap can be so effective in the initial capture process.

The reason for the inability to produce  $\text{Sm}^{3+}$  reduction by uv, or 1.5-MeV electrons, can only be speculated upon. Perhaps the position of the  $\text{Sm}^{3+}$  ion within the complex reduces its opportunity for electron capture.

Bleaching probably progresses in the following manner. Infrared excitation promotes capture of an electron by the interstitial fluorine atom. Nonradiative electron-hole recombination then occurs from the  $\text{Y}^{2+}$  ion.

#### ACKNOWLEDGMENTS

The author wishes to express grateful appreciation to Dr. H. H. Theissing and P. J. Caplan, USAEL, for their encouragement and helpful comments.

<sup>8</sup> W. J. Scouler and A. Smakula, Phys. Rev. **120**, 1154 (1960).