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Color Center Production in $CaF_2Sm^{3+}(Y^{3+})$ by Ultraviolet Irradiation

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Color centers have been produced in certain CaF_2Sm^{3+} crystals by ultraviolet irradiation. The color centers are attributed to reduction of Y^{3+} impurities. Although no 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 $CaF_2:Sm^{3+}$, 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 ~2700 Å. Irradiation into this edge, or at shorter wavelengths, rapidly produced coloration. The color center is identified as Y^{2+}.[1] Y^{3+} is a common impurity in fluorite starting materials.

Y^{3+}[1] and Sm^{3+}[2] in 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, Y^{3+} reduction was reported to be completely suppressed by small quantities of Sm^{3+}. In our crystals, however, even though no direct participation of Sm^{3+} in the coloring process was noted, its presence was indispensable for reduction of the Y^{3+}.

(2) High-energy irradiation was found[2] to be effective in the reduction of Sm^{3+} in 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 Sm^{3+} reduction was observed in our crystals, although Y^{3+} reduction was easily accomplished by appropriate uv irradiation. A crystal was exposed to 1.5-MeV electrons and although the Y^{2+} color centers were rapidly formed, no significant 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 ~4200 and 6300 Å and the sharp line at 6900 Å are due to the divalent samarium ion.[3]

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

(3) A broad line at ~2550 Å believed to be due to Sm^{3+} ion-pair resonance absorption.[4,5]

(4) A very intense, rather steep, absorption edge from ~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 Sm^{3+} lines at ~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

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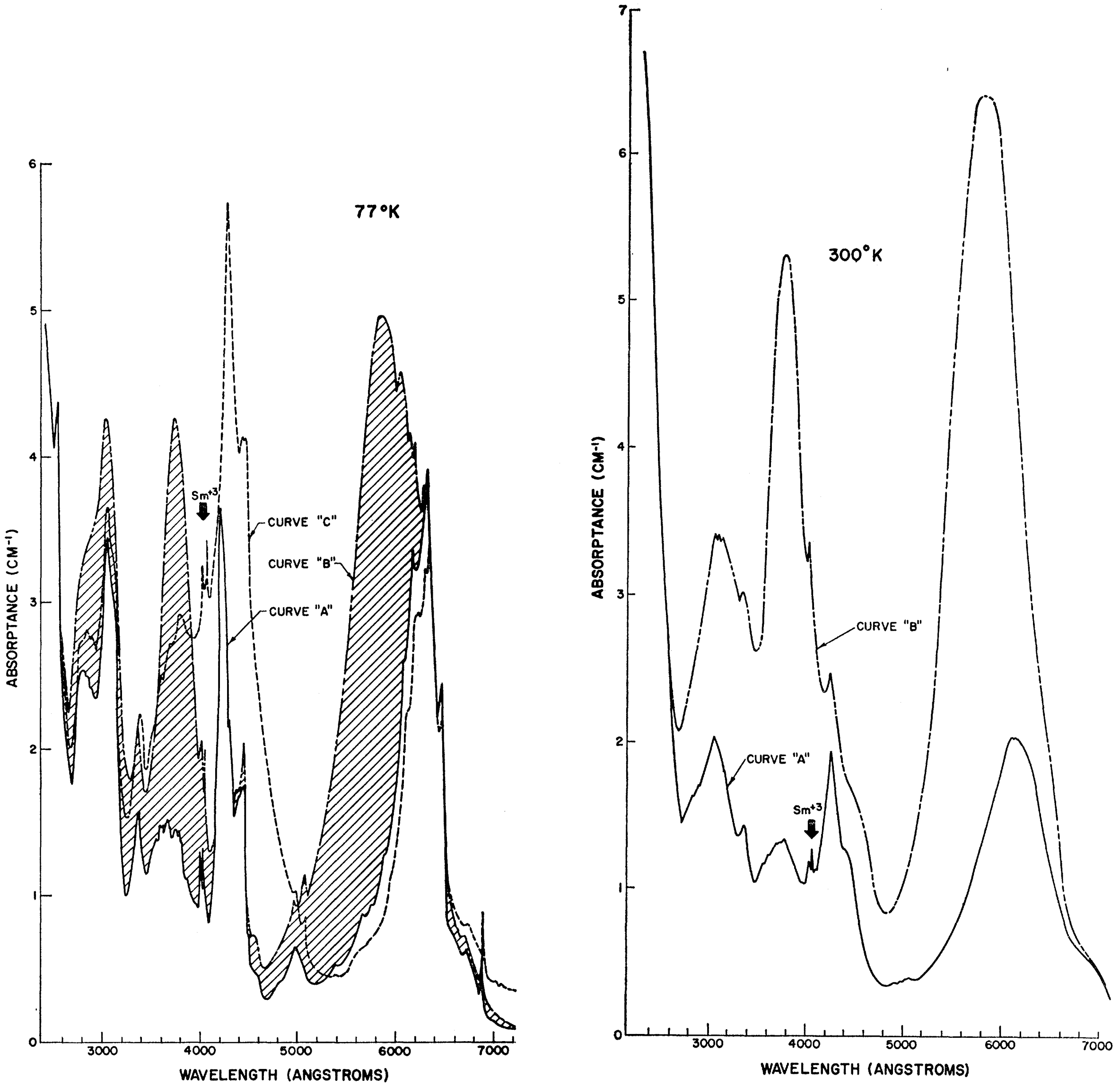
[1] J. R. O'Connor and J. H. Chen, Phys. Rev. **130**, 1790 (1963).

[2] J. R. O'Connor and H. A. Bostick, J. Appl. Phys. **33**, 1868 (1962).

[3] W. Kaiser, C. G. B. Garrett, and D. L. Wood, Phys. Rev. **123**, 766 (1961).

[4] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).

[5] G. H. Dieke and E. Dorman, Phys. Rev. Letters **11**, 17 (1963).



(a) (b)

Fig. 1. (a) and (b). Absorptance at 77 and 300°K of a CaF_2:$Sm^{3+}(Y^{3+})$ crystal in various stages of coloration. In both figures, curve A represents normal absorptance and curve B is absorptance after coloration. Curve C is discussed in the text.

that the original spectrum is substantially changed. A broad underlying band at ~3900 Å and a low tail from ~6500 to 8500 Å 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 ~3000, 3800, and 5800 Å. These bands are identified as three components of the Y^{2+} spectrum.[1] The fourth component, which would be expected at ~2250 Å, 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.[1]

DISCUSSION

A search was made of available CaF_2: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" CaF_2:Sm^{3+} fluorescence spectrum.[6] Absorption curves made of these crystals showed more or less evidence of the Sm^{3+} and 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 Sm^{2+} content) the edge started at ~2700 Å. In clear crystals (virtually no Sm^{2+} content, which is indicative of oxygen contamination[7]) the edge receded ~200 Å toward shorter wavelengths.

Since coloration did not alter the character or intensity of the 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 Sm^{3+} ions are not visibly affected during the processes, their presence is indispensable for uv induced 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 Sm^{3+}, Y^{3+}, and a third component which is ionized by uv irradiation.

Y^{3+} impurities in CaF_2 are known to be closely associated with F^- interstitials.[8] Presumably, the trivalent ion is charge compensated by an F^- interstitial in a neighboring position. Perhaps the effect of the 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°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 Sm^{3+} reduction by uv, or 1.5-MeV electrons, can only be speculated upon. Perhaps the position of the 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 Y^{2+} ion.

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

[7] H. Guggenheim, J. Appl. Phys. **32**, 1337 (1961).

[8] W. J. Scouler and A. Smakula, Phys. Rev. **120**, 1154 (1960).