Optical Absorption Bands in γ-Ray Irradiated LiF Crystals

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The color centers produced in LiF crystals by γ-rays from Co^{60} have been investigated. The time rate of increase of F-centers diminished with continued γ-ray irradiation and that of M-centers was constant as far as the F-center concentration was lower than $2\times10^{18}/cm^3$, and further there was a squar relation between the densities of both centers. The band at 220 mμ was developed remarkably in some crystals by the exposure to F-band light and not at all in other crystals.

INTRODUCTION

The absorption bands caused by crystal defects in various alkali halide crystals have been extensively studied[1], and the correspondence among the absorption bands in these crystals is fairly clear. In the case of LiF, such a correspondence is not so clear for some of the absorption bands owing to the following reasons : pure crystals are difficult to be obtained, various absorption bands are apt to be produced by ionizing radiation, additive coloration has not been realized in LiF crystals, and V-type bands of the crystals, which would lie on the region below 200mμ, are difficult to be treated with ordinarly spectrophotometer. Above all, it has been considered that the appearence of the absorption band at 220 mμ after the bleaching of F-band by F-light or thermal treatment, which was reported by Delbecq and Pringsheim, is peculiar to LiF crystals[2]. We have investigated the absorption bands produced in γ-ray irradiated LiF crystals and examined whether these bands were characteristic or not.

In alkali halide crystals, the models of electron trapped centers have not yet been consistently established except for F-centers. As for M-center, which has been recognized as the association of one F-center and an adjacent pair of anion and cation vacancies, Overhauser and Ruechardt conceived in their Stark effect experiments that the above M-center model proposed by Seitz would be necessary to be revised[3]. In spite of many experiments for M-centers, there have been few researches concerning M-center production by ionizing radiation. Then, in order to clarify the relation between F- and M-centers, we have observed the concentration of M-centers as a function of that of F-centers in γ-ray irradiated LiF crystals.

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EXPERIMENTAL METHOD

LiF materials were purified and prepared in our laboratory from LiCl and NH_4HF_2, and single crystals were produced by Kyropoulos' method in flowing dry nitrogen gas of about 50 mm Hg pressure[4]. The crystals used in the present work were classified into three species named crystals I, II and III according to preparation process and crystal growth condition. The intensity of the ultraviolet absorption, which was designated as "A absorption" by the authors[4], was weaker in crystal I than in the other two, in which the intensities of this absorption were comparable.

The samples with thickness of approximately 0.3~3 mm were cleaved from the crystals and coloration was produced at room temperature by γ-ray from Co^{60} giving 2×10^5 roentgens per hour at the Institute for Chemical Research of our University. The optical absorption was measured at room temperature by Beckman DU spectrophotometer.

RESULTS AND DISCUSSIONS

(a) F- and M-Band

In the early stage of the coloration (at about one hour γ-ray irradiation), F-band at 250 mμ, a broad and weak band with a maximum at 350 mμ and much weaker M-band at 450 mμ were produced. The latter two bands gave a light yellow color to irradiated crystals. A prolonged γ-ray irradiation (for example, about 8 days) produced intense M-band and two weak bands with

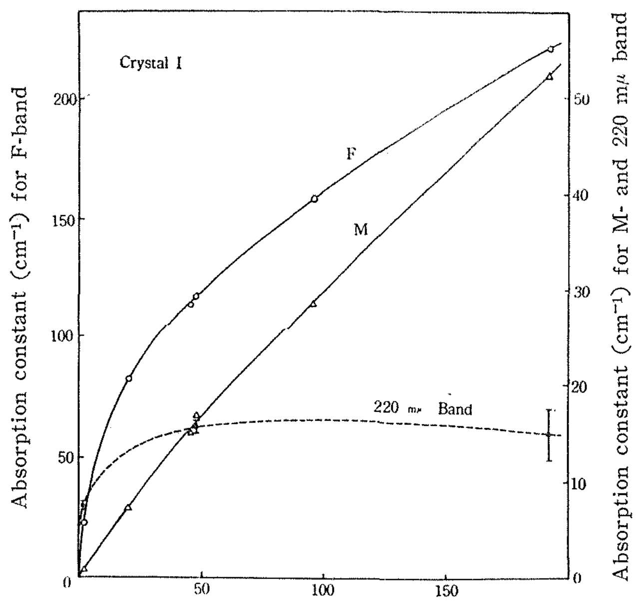

Fig. 1. Absorption constants of F-, M- and 220 mμ bands as function of γ-ray irradiation time.

peaks at about 320 mμ and 380 mμ in addition to the enhanced F-band. These two bands were tentatively classified as R_1- and R_2-band respectively by Penneman and powers[5]. In this stage of the coloration, the crystal showed brown or dark brown color mainly due to M-band. Immediately after a brief irradiation, F'-band with a peak at 620 mμ was observed, but this band was unstable at room temperature and the prolonged irradiation did not increase further this band intensity.

Fig. 1 shows the absorption constants of F- and M-band as a function of irradiation time; F-band increases very rapidly in early stage of irradiation, and after about 20 hours, the rate of increase of this band decreases. In the X-rayed alkali halide crystals F-band is easily saturated, but in the case of LiF crystals F-band is not saturated even at the concentration of $2\times10^{18}/cm^3$, which is estimated from the Smakula's formula by assuming the oscillator strength of this band to be unity. As for M-band, its intensity is in general proportional to irradiation time. The relation between the concentrations of F- and M-centers is shown in Fig. 2, and from this figure, as far as the F-center concentration is lower than $2\times10^{18}/cm^3$, the relation can be expressed approximately as the following empirical formula :

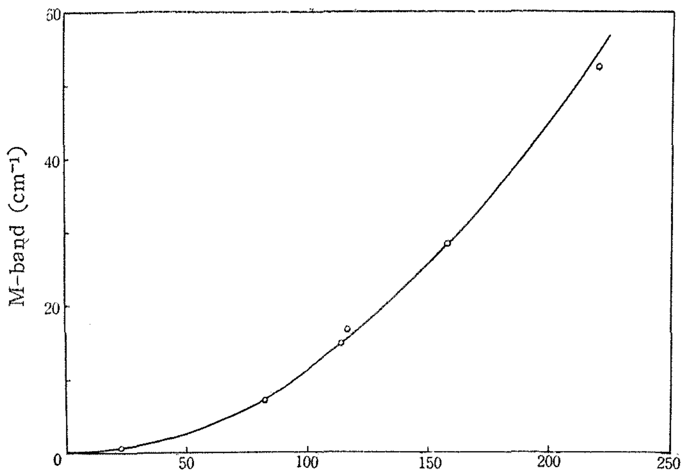

Fig. 2. The relation of absorption constants between F- and M-bands in γ-ray irradiated LiF crystals.

$$[F]^2 = k[M],$$

where k is a constant and the brackets represent the concentration of F- and M-centers. And if the brackets are expressed in absorption constant (cm^{-1}), k is about 890, but, of course, it would take a different value according to irradiation conditions, for instance, the temperature of the crystals under irradiation.

(b) 220 mμ Band

When the crystal I irradiated by γ-ray was exposed to the light from a low pressure mercury lamp through KI crystal filter of about 1 mm in thickness (the light of wavelength 254 mμ was intense and the light of shorter wavelength than 250 mμ was almost absorbed by the filter), the F-band intensity was gradually reduced and the F-band peak shifted to the shorter wavelength side and finally settled down at 220 mμ. Fig. 3 shows the bleaching effect of the γ-rayed LiF crystal I.

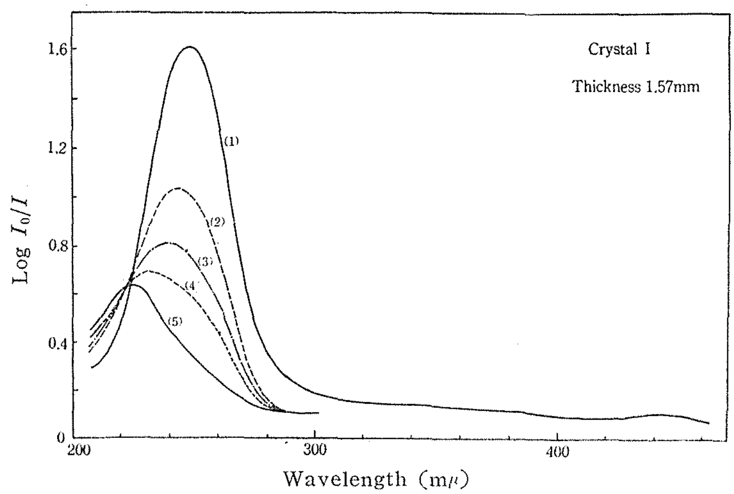

Fig. 3. F-band bleaching in LiF crystal I.
(1) 100 minutes γ-rays at room temperature. (2) 13 hours, (3) 7 hours, (4) 7 hours, and (5) 21 hours successive F-light irradiation at room temperature.

This band at 220 mμ is the same as that reported by Delbecq and Pringsheim[2], but when the crystal had higher concentration of F-centers by a prolonged exposure to γ-rays, the height of 220 mμ band relative to that of origin-

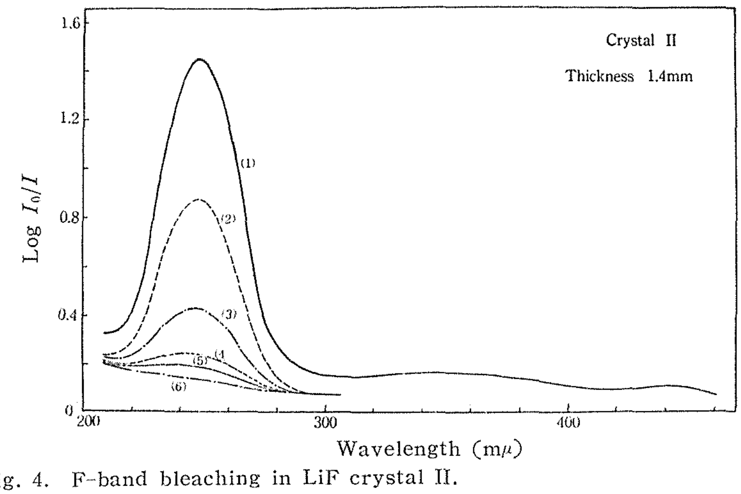

Fig. 4. F-band bleaching in LiF crystal II.
(1) 100 minutes γ-rays at room temperatur. (2) 9.5 hours, (3) 20 hours, (4) 14 hours, (5) 7 hours, and (6) 28 hours successive F-light irradiation at room temperature.

al F-band was lowered, as Morehead and Daniels noticed in the case of LiF crystal irradiated by alpha-particles[6]. The relation between the intensities of original F-band and that of 220 mμ band is shown in Fig. 1.

Contrary to the case of the crystals I, this 220 mμ band did not remain at all in the crystals II, as shown in Fig. 4, and was barely detectable in the crystals III, for the same bleaching procedures and nearly the same concentrations of F-centers as those of the crystals I.

Before the exposure to γ-rays, the intensity of A absorption of the crystal I is lower than those of the others, as mentioned above but the relation between the existence of A absorption and the appearence of 220 mμ band after γ-ray irradiation is not yet clear. Nevertheless, the result that there is the tendency of saturation in formation and the diversity of intensity in each crystal for 220 mμ band might suggest the following fact; the electrons released from F-centers are captured by some impurity atoms, or anion vacancies decomposed from F-centers are combined adjacent to the foreign atom sites, and then 220 mμ band is induced. If 220 mμ band is not intrinsic in LiF crystals, the singularity of color centers in this crystal will be reduced.

(c) 350 mμ Band

In the early stage of γ-ray irradiation, the broad band with a peak at 350 mμ was produced, and after attaining to some intensity, the band was no more developed by the prolonged γ-ray irradiation. This band was relatively unstable at room temperature and easily destroyed by the light from a mercury lamp. This band is so broad, as shown in Fig. 5, but this seems to be a single band since it is uniformly weakened by the monochromatic light of wavelength 365 mμ. It is considered that this band might also be an absorption induced by

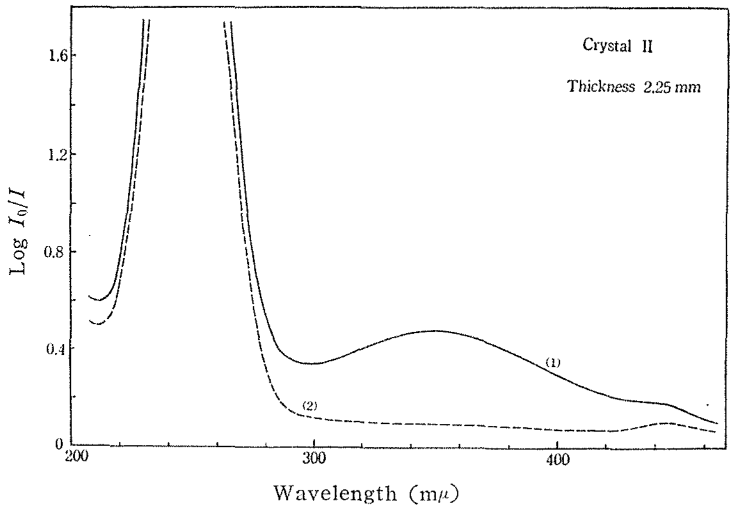

Fig. 5. 350 mμ band in γ-ray irradiated LiF crystal.
(1) 75 minutes γ-rays at room temperature. (2) 2 hours bleached by the light of the mercury lamp at room temperature.

some impurity centers contained in the crystals, but further detailed experiments will be necessary for conclusive decision.

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