Relative Concentration of F, M and R Centers

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Relative concentrations of the F, M and R centers in alkali halides have been invesitigated, over a wide range of absorption intensities, on the crystals of LiF, LiF(Pb) and LiF(Mg) which were irradiated with γ-rays at room temperature. In early stages of the coloration, the M-center concentration is proportional to square of the F-center concentration and the R-center concentration to cube of the F-center concentration except for the LiF(Mg) which shows an intermediate band on the long-wavelength side of F band after the γ-ray irradiation. Some deviation from the above relationship is observed in a high-concentration range where higher coagulation of the centers is likely to happen. The M- and R-center models of van Doorn and Pick have been supported by the results.

INTRODUCTION

In alkali halides, F centers are produced primarily by room-temperature irradiation and M, R and N centers in turn by prolonged irradiation. Seitz[1] suggested first the models of these complex centers (Fig. 1): the M center consists of an F center associated with a neutral vacancy-pair and the R_1 and R_2 centers consist of a pair of negative-ion vacancies associated with one and two electrons, respectively. From the recent studies on these centers, however, some different interpretations of the models were put forward[2,3]: the M center is a pair of F centers (R_2 model proposed by Seitz) and R_1 and R_2 bands are due to transitions in the same center which consists of three F centers (see Fig. 1).

In the thermal equilibrium of the F and M centers in additively colored crystals, van Doorn[4] has shown that the M-center concentration varies quadratically with the F-center concentration. In the crystals γ-rayed at low temperature, Faraday et al.[5] have pointed out the same relation between the F and M centers and a cubic relation between the F and R centers. They considered that the above results support the F_2 model of M center and the F_3 model of R center, respectively. The square relation between the F and M centers has been pointed out in earlier report by Fukuda and Okuda[6]. Since the results of concentration of these centers may give important information in connection with the
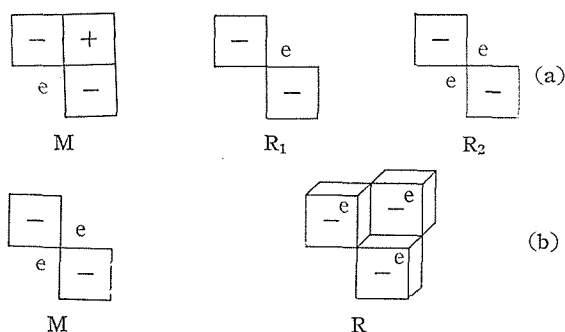
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Fig. 1. (a) The M-, R_1- and R_2-center models of Seitz.
(b) The M- and R-center models of van Doorn and Pick.

decision of the models, the present paper will deal with the relative concentrations between them, extending the range of the concentration and reexamine the results.

EXPERIMENTAL PROCEDURE

LiF crystals were produced in a vacuum-type furnace and Pb- or Mg-doped (1 mol%) LiF crystals were produced by the ordinary Kyropoulos method. The crystals were exposed at room temperature to γ-rays from Co[60] giving 1.3×10^6 roentgens per hour and the exposure times were varied from one hour to three weeks to obtain suitable concentrations of color centers. In order to measure the optical density of the crystals with high concentration of centers, some crystals were cleaved into plates with about 0.07 mm in thickness and the light for absorption measurement was focused on small area of the thin crystals, using a modified Shimadzu QR spectrophotometer.

The relative concentrations of the centers were obtained from peak intensities of the absorption bands measured at room temperature. In LiF, the F, M R_1 and R_2 bands locate at 248, 447, 320 and 378 mμ, respectively[3], and the R centers were estimated with the R_2 band whose resolution from adjacent bands was better than that of the R_1 band. In addition to the above absorption bands, a weak and broad band with peak at 350 mμ appeared immediately after the γ-ray irradiation, but this band was so unstable that it was bleached out, scarcely affecting the F, M and R bands, by a brief exposure to ultraviolet light (365 mμ)[6]. Assuming that oscillator strength for the F band is unity and refractive index is 1.4, the highest concentration of the F centers is estimated to be about 3×10^{18}/cm^3.

RESULTS AND DISCUSSION

Figs. 2 and 3 give logarithmic plots of the absorption constants of the F, M and R bands induced in the pure and doped LiF crystals by the γ-ray irradiation. Fig. 2 refers to the relation between the F and M bands; Fig. 3 to the relation

between the M and R bands. The results of pure and Pb-doped crystals show that the relative concentration of these centers may be approximately expressed, over a wide range, by

$$[N_M] = k[N_F]^2 ; \qquad [N_R] = k'[N_M]^{3/2} = kk'[N_F]^3, \qquad (1)$$

where k and k' are constants and may be dependent upon the irradiation conditions. In fact, the values of k and k' in γ-ray irradiated crystals markedly differed from the values in β-ray irradiated crystals. Although the concentration
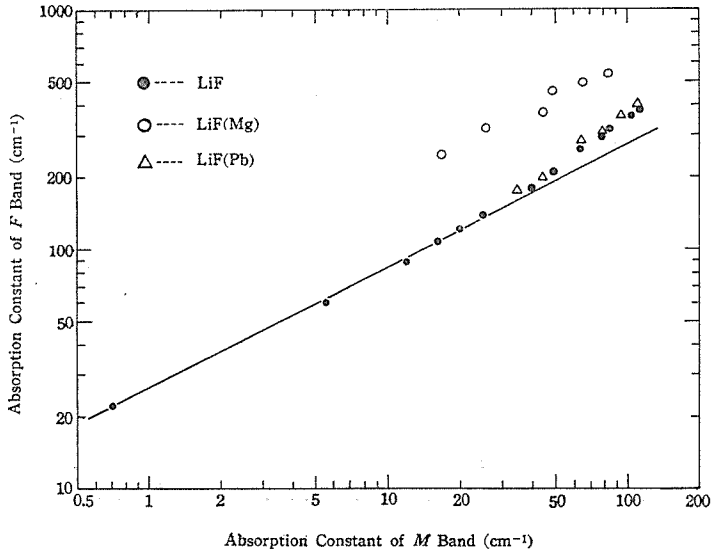
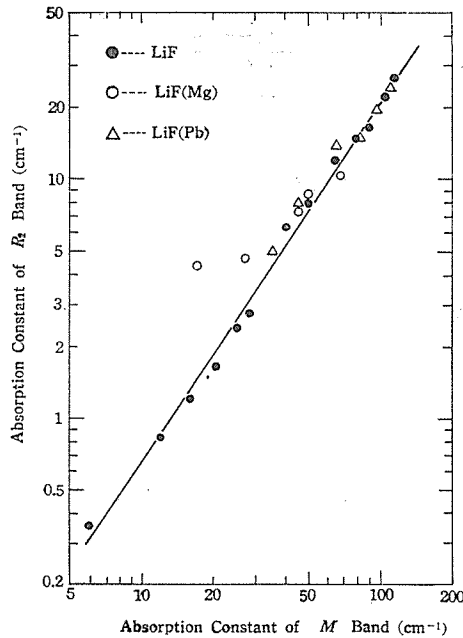Fig. 2. Absorption constants of the F and M bands in γ-ray irradiated LiF.

Fig. 3. Absorption constants of the R_2 and M bands in γ-ray irradiated LiF.

of the M centers does not vary quadratically with that of the F centers in the higher concentration range in Fig. 2, this may be attributed to a conversion of the M centers into the R centers. It should be mentioned that an appreciable N band has not appeared in the crystals investigated. The F centers in Pb-doped crystals were more easily produced than those in pure crystals and the phenomenon that the time rate of F-center production is enhanced in doped crystals has been observed in other alkali halides[7]. In the Mg-doped crystals, relative concentration of the centers appears to deviate from the above formula. This deviation may be connected with an intermediate band which apprears on the long-wavelength side of the F band after the γ-ray irradiation and disappears with an exposure to ultraviolet ligh (253 mμ~280 mμ) as shown in Fig. 4. Thus it is seen that the relations (1), which are in agreement with the previous data, hold in the lower concentration range where a higher coagulation of the centers is unlikely to succeed.
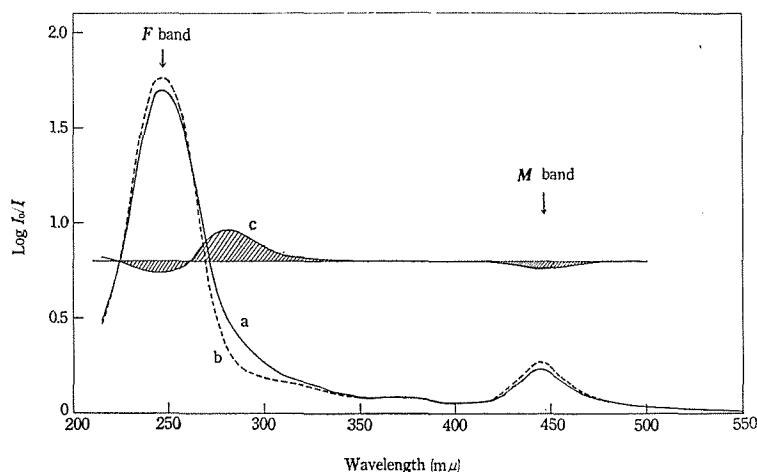

Fig. 4. Absorption spectra of Mg-doped LiF crystal. (a) After exposure to γ-rays. (b) After subsequent irradiation with an ultraviolet light (~280 mμ) at room temperature. (c) Difference between (a) and (b), indicating an intermediate band with a peak at 280 mμ.

Implication of the experimental results will be discussed on the assumption that the M center consists of a pair of F centers and the R center consists of three F centers, according to van Doorn and Pick. In a concentration range where the R centers are not yet produced, the number of M centers produced in a time interval dt, dN_M, is connected with the F-center concentration N_F, and the number of F centers produced in the time interval, dN_F, as follows,

$$dN_M = CN_F(dN_F + 2dN_M)$$

where C is a constant. Since it is reasonable to assume $CN_F \ll 1$, we obtain the M-center concentration,

$$N_M = \frac{1}{2} CN_F{}^2 + \cdots\cdots. \tag{2}$$

Similarly, in a range where the N centers are not yet produced, the number of R centers produced in a time interval is connected with the numbers of F and M centers produced in the time interval and the M-center concentration,

$$dN_R = C'N_M(dN_F + 2dN_M + 3dN_R),$$

where C' is a constant. Assuming $CN_M \ll 1$ and $C'N_M \ll 1$, the R-center concentration is given by using (2):

$$N_R = \frac{\sqrt{2}}{3} \frac{C'}{\sqrt{C}} N_M^{3/2} + \cdots\cdots. \tag{3}$$

It is seen that, in the range where higher coagulation of the centers does not happen, Eqs. (2) and (3) agree with the experimental results of low-concentration range. From the investigation on anisotropic absorption and emission of the M and R bands, it has been shown that the M center has its symmetry axis lying along the face diagonal of the crystal; and the R-center along the body diagonal of the crystal[2,3]. In company with this, therefore, the present results will give to support the proposal of the F_2 model for the M center and the F_3 model for the R center. Further, the results of Pb- or Mg-doped crystals show that the existence of positive-ion vacancies seems to be not important for the M- and R-center productions as suggested by Faraday et al.. However, the evidence that the F_2 or F_3 model does not accompany any vacancies is not deduced from the present results.

ACKNOWLEDGMENTS

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