Determination of color centers in CaF_2 crystals by multiple gamma-ray irradiations

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Color centers of CaF_2 crystals subjected to three high-dose gamma-ray irradiation treatments were studied. Three absorption bands at 349, 409 and 478 nm are ascribed to the F interstitials through the variation in difference additional absorption values. The transformation of interstitial F atoms to F ions (F_i^-) is demonstrated using data with increasing radiation dose. The decrease in the 600 nm absorption band and the occurrence of the 580 nm band correspond to F_2^+ center conversion to F center. The complex (F^--F_i^0) might be associated with the 962 and 1196 nm bands.

CaF_2 , TGT, gamma-ray, irradiation, color centers, crystals

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As a representative alkaline earth fluoride, calcium fluoride (CaF_2) single crystals have been the subject of experimental and theoretical studies for years. Extensive studies have been performed on the color centers of these crystals. The color center is a region in the transparent crystal with point defects; point defects or point-defect clusters able to trap electrons or holes constitute a defect. F color center formation arises because of the capture of the electrons of the anion vacancy. The color centers in calcium fluoride are quite different from those in alkali halides because of the different lattice structures and especially the presence of interstitials in addition to vacancies. However, the color centers vary widely with coloration method (such as additive coloration in Ca vapor or by irradiation with electrons, X-rays, γ -rays or neutron), crystal origin, and impurity content. Gamma irradiation is an effective method to produce color centers in CaF_2 crystals and its radiation effects on CaF_2 crystals have been studied using optical absorption [1,2] and thermoluminescence [3]. Compared with other coloration methods, exposure of CaF_2 crystals to gamma-

ray radiation produces many types of color centers, which makes the determination of the true nature of color centers relatively difficult. We found, however, that multiple gamma-ray irradiation could be an effective method to determine color centers in CaF_2 crystals. Previous researchers have found that radiation could induce thermoluminescence in CaF_2 [4] and its optical properties were unaffected [5]. Nevertheless, they did not explicitly examine the transitions in the color centers caused by increasing the radiation dose. For this paper, related experiments and data analysis have been done to examine the F color center conversion by controlling irradiation dosage.

1 Experiments and results

Pure CaF_2 single crystals were grown by temperature gradient techniques (TGT) which had been discussed in detail previously [6,7]. To eliminate the oxygen contamination during crystal growth, the starting materials of CaF_2 powder was mixed with about 2 wt% PbF_2 powder, which would be released from the crucible prior to the growth process to

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prevent hydrolysis. Samples of 2.24 mm thickness were cut from the as-grown CaF_2 crystals perpendicularly to the growth axis and then polished on both sides. Next, the samples were subjected at room temperature to three treatments of radiation using a ^{60}Co gamma ray source (average gamma energy 1.25 MeV) up to an absorbed dose of 2×10^6 rad and 2×10^7 rad with dose rate of about 170 Gy/min and 2×10^8 rad with dose rate of about 250 Gy/min. The absorption spectra were recorded using a V-570 UV/VIS/NIR spectrophotometer.

As-grown CaF_2 crystal is colorless, but after a 2×10^7 rad exposure, it turns to light brown and then to deep brown with further irradiation. This irradiation-induced color can be thoroughly bleached in air by increasing the temperature to 160°C (Figure 1).

Figure 2 shows the absorption spectrum of as-grown and gamma-irradiated CaF_2 crystals. No color centers are seen in the as-grown CaF_2 crystals before radiation; intrinsic absorption bands cause the increase in absorption toward shorter wavelengths. After gamma irradiation, six main color-center absorption bands appear which peak at about 262, 365, 391, 456, 506, and 551 nm. These results are quite different from the well-known four bands at 225, 335, 400 and 580 nm of CaF_2 crystals with coloration produced by X-rays [8,9], high-energy electrons (2.5 MeV) [10] and γ -rays [1].

In addition to the six absorption bands, two weaker shoulder peaks at 215 nm and 600 nm appear at the short-wavelength side of the 262 nm band and long-wavelength side of the 551 nm band.

To examine the dependence of the color centers on the absorbed gamma-ray dose, we performed a further two irradiation treatments with doses 2×10^7 rad and 2×10^8 rad on the same sample. The absorption spectra are shown in Figure 2(c) and (d). Nearly all absorption band intensities increased after irradiation but this increase is not proportional to the radiation dose.

To clearly show the new absorption bands and the dependence of color centers on absorbed dose, we calculated difference additional absorption (DAA) which is defined as: $\Delta S = a_2 - a_1$, where a_1 and a_2 are the absorption coefficients of CaF_2 crystal irradiated by different doses. The DAA curves of S_{10} , S_{21} , S_{32} , and S_{31} presented in Figure 3(a), (b), (c), and (d); the subscripts 0, 1, 2, and 3 denote radiation doses 0 rad, 2×10^6 rad, 2×10^7 rad, and 2×10^8 rad respectively. Note that the figure can be divided in terms of DAA values into three regions, labeled I, II and III. In region I, as radiation dose increases, the absorption intensity increases and nearly reaches saturation after the 2×10^8 rad irradiation. This suggests that the color centers in this region become saturated as radiation dose increases. Three abnormal bands

Figure 1 Color of the CaF_2 crystals after gamma irradiation and annealing.

Figure 2 Absorption spectrum of the as-grown (a) CaF_2 crystal, and 2×10^6 rad (b), 2×10^7 rad (c), and 2×10^8 rad (d) γ -irradiated CaF_2 crystals.

Figure 3 DAA spectrum after 2×10^6 rad, 2×10^7 rad, and 2×10^8 rad gamma irradiation.

at 349, 409, and 478 nm were found in region II. The absorption intensities of these bands increase after the 2×10^6 rad and 2×10^7 rad irradiation but decrease after the 2×10^8 rad irradiation. This indicates color-center transformations occur during irradiation. There is an exception though in that the 380 nm band increased overall. In region III, one new band at 580 nm, which is absent in the 2×10^6 rad and 2×10^7 rad γ -irradiated crystals, occurred when exposed to a 2×10^8 rad radiation dose, specifically, the sample treated to initially 2×10^7 rad irradiation and subsequently 2×10^8 rad irradiation. In addition, one small absorption band appears at 962 nm and increases after both 2×10^7 rad and 2×10^8 rad radiation doses, and another at 1186 nm after a 2×10^8 rad radiation dose, both of which are inconsistent with the results obtained by Alvarez et al. [1] of bands at 780 and 1025 nm.

2 Discussion

Considering the color-center saturation in region I, the color centers seem to be associated with oxygen impurity defects. Oxygen has been shown to exist in CaF_2 crystals in the combinations $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OH})\text{F}$, CaO and Ca_2OF_2 [10]. Although 2 wt% PbF_2 has been added to the CaF_2 crystals to eliminate oxygen contamination, removing oxygen completely is difficult. Oxygen is a highly electronegative element ($X_{\text{O}}=3.5$) and traps electrons during irradiation until the point of saturation.

Because of the small atomic radii ($R_{\text{F}}=67$ pm, $R_{\text{Ca}^{2+}}=100$ pm, $R_{\text{F}^-}=113$ pm), a large number of F atom interstitials exist in CaF_2 crystals. Previous studies have suggested that the 400 nm was correlated with neutral interstitial F atoms. Our experimental results further indicate that the 349, 409, and 478 nm bands are associated with the same type of defect. The 409 nm band is very close to the 400 nm band and we conclude that the 349, 409, and 478 nm bands are associated with F interstitials. As usual, gamma-ray irradiation cannot lead to atom displacements. Consequently, it is very possible interstitial F atoms trap electrons to form F ion (F_i^-) interstitials. The decrease in the 349, 409 and 478 nm bands is ascribed to this transformation. The 380 nm band in region II is quite close to the 375 nm band, which corresponds with the F center obtained by Arends [11] and the slight difference appears to be due to a perturbation of the center by impurities or imperfections in the various crystals.

Why did the 600 nm band appear after 2×10^6 rad irradiation then decrease and vanish after two subsequent high-dose irradiations? Why did the 580 nm band appear when the sample was exposed to a high-dose irradiation? The reasons could be as follows: As previously reported by Scouler [12], the 580 nm band very probably corresponds to electrons trapped in anion vacancies and, because of the presence of Na^+ ions, the 580 nm band shifts to 605 nm in NaF-doped CaF_2 crystals. Smakula and Messner [10] showed that the 580 nm band in electron-beam-colored

CaF_2 crystals shifted to 600 nm with decreasing temperature to -190°C . These results clearly indicate that the 580 nm and 600 nm bands are both associated with electron-trapped anion vacancies but belong to different kinds of F^- -type color centers. The variation in the absorption intensity after gamma irradiation (Figure 4) indicates that these two bands belong to different kinds of F^- -type color centers. F_2^+ center pairings in CaF_2 have been shown to be stable and can be formed by the capture of a F^+ center by an unstable F at room temperature [13]. After 2×10^6 rad irradiation, almost all F centers in CaF_2 crystals are transformed to F_2^+ centers, which contribute to the 600 nm band by capturing neighboring F^+ center. With the 2×10^7 rad and 2×10^8 rad irradiations, excess electrons produced in CaF_2 crystals would be trapped partly by the remaining F^+ centers to form F centers, which is the reason why the 580 nm band appears and the intensity in the 600 nm band decreases. In contrast, the F centers are still unstable and would trap F atom interstitials to form the relatively stable (F^--F_i^0) complex. This complex might be associated with the 962 and 1196 nm bands.

The preceding also explains well the occurrence of the 600 nm band in electron-beam-colored NaF-doped CaF_2 crystals at room temperature and pure CaF_2 crystals at low temperature. Doping CaF_2 crystals with NaF has the effect of generating a large number of F^- vacancies through charge compensation and F center-trapped F^- vacancies to form F_2^+ center. At low temperature, the lattice constant is reduced and the F center has a larger probability of binding with an F^+ center by electron irradiation to form the 600 nm F_2^+ center band.

3 Conclusions

In conclusion, the appearance of the 349, 409, and 478 nm absorption bands is ascribed to the F interstitials. The decrease in these three bands upon higher radiation doses is

Figure 4 Absorption spectra of gamma irradiated CaF_2 after annealing at different temperatures.

due to the transformation of F atom interstitial to F ion (F_i^-). The appearance of the 600 nm absorption band was due to the formation of F_2^+ centers after the 2×10^6 rad gamma irradiation. With F_2^+ centers transforming to F centers, the 600 nm band decreased and the 580 nm band appeared after higher-dose irradiation. The complex ($F^-F_i^0$) might be associated with the 962 and 1196 nm bands, but the result remains tentative until a further study is completed.

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