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Effect of Optical and Thermal Bleaching on the uv Bands in Highly Pure and Mn-Doped KCl Crystals

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In highly pure KCl crystals, x irradiated at room temperature (RT), the usual uv absorption bands at 212 and 230 nm are observed. The peak position of the 212-nm band when bleached with uv light shifts gradually to 195 nm, without any appreciable change in the intensity of this band. On thermal bleaching (in the range RT to 150°C) in the dark, the position and the intensity of the 212-nm band remain unchanged. When bleached thermally or optically with uv light, the peak position of the 230-nm band remains unaltered, whereas its intensity decreases. In uncolored KCl:Mn crystals, Mn introduces two uv absorption bands at 201 and 273 nm, having half-widths 0.36 and 0.15 eV, respectively. On x irradiation, the positions, intensities, and half-widths of these absorption bands remain unaltered, and a new absorption band at 223 nm appears. The intensity and half-width of the 223-nm band increases up to 25 h of x irradiation. Although thermally unstable, the centers responsible for the 223-nm band are fairly resistant to uv-light bleaching. An activation energy $E_a = 0.54 \pm 0.02$ eV is obtained for the thermal bleaching of the centers that absorb in the 223-nm band. Qualitatively, the 223-nm band is similar to the D bands observed by Ishii and Rolfe.

1. INTRODUCTION

IONIZING radiations in alkali halides generate, in addition to the F and F-aggregate bands in the visible, various absorption bands due to the trapping of holes in the uv region, known as V bands.[1] EPR measurements have conclusively established that some of the uv bands formed during the irradiation process are due to electron-deficit halogen-molecule centers which are complementary to the F centers in one way or the other.

Irradiating the pure KCl crystals at room temperature (RT) generates in the uv region the V_2 and V_3 bands having peaks at 230 and 212 nm, respectively. The V_3 band in pure KCl crystals has been attributed to a Cl_3^- molecular ion at a cation vacancy.[2,3] Lüty[4] and Damm and Tompkins[5] have attributed the V_2 and V_3 bands to the presence of impurities. Nadeau[6] has observed that these bands do not appear in crystals having considerably reduced impurity content. Zaleskiewicz and Christy[7] have shown that the V_3 band is very resistant to the uv-light bleaching at RT; however, in the vicinity of 100°C this band bleaches at an appreciable rate.

The presence of impurities such as copper[8] and alkaline earth metals[9] also give absorption bands in the uv region, very similar to the V bands. These have been designated as D bands by Ishii and Rolfe.[9] These impurities are known[9] to enhance the magnitude of the V bands and modify their nature and position.

We present in this paper some interesting observations of the effects of optical and thermal bleaching on the uv bands in x-irradiated, highly pure, and Mn-doped KCl crystals.

2. EXPERIMENTAL

Single crystals of highly pure KCl (spectroscopically analyzed pure material was obtained from Johnson Matthey and Co., London, and contained background divalent cation impurity $\lesssim 1$ ppm) and Mn-doped KCl were grown from the melt in the laboratory by the Kyropoulos method. The concentration of Mn in the doped crystals was analyzed chemically and was found to be approximately 1/100 of the amount added to the melt. The letters H and E denote the crystals grown from highly pure KCl and Mn-doped KCl materials, respectively. E1, E2, and E3 denote, respectively, crystals containing 50, 100, and 200 ppm of Mn in KCl.

Crystals with higher concentration of Mn impurity (>200 ppm) were translucent or opaque, even after quenching from high temperatures. Moreover, crystals with higher impurity concentration could not be grown without deterioration in quality. For this reason no work has been done with crystals containing more than 200 ppm of Mn.

Blocks of approximately 1 cm^3 were cleaved from the central part of the large crystals. The blocks thus obtained were then quenched from 650°C, after having been kept at that temperature for 2 h. For optical absorption measurements, thin slices, approximately $10 \times 10 \times 0.5$ mm, were cleaved from these blocks.

X irradiation was done at RT with a Philips PW 1009 x-ray diffraction unit, using a Mo target and operating at 35 kV and 10 mA. The slices were irradiated through the broad face. A thin KCl filter (0.3 mm thick) was used to cut the effect of soft x rays. The dose rate at the crystal position was measured by an R meter

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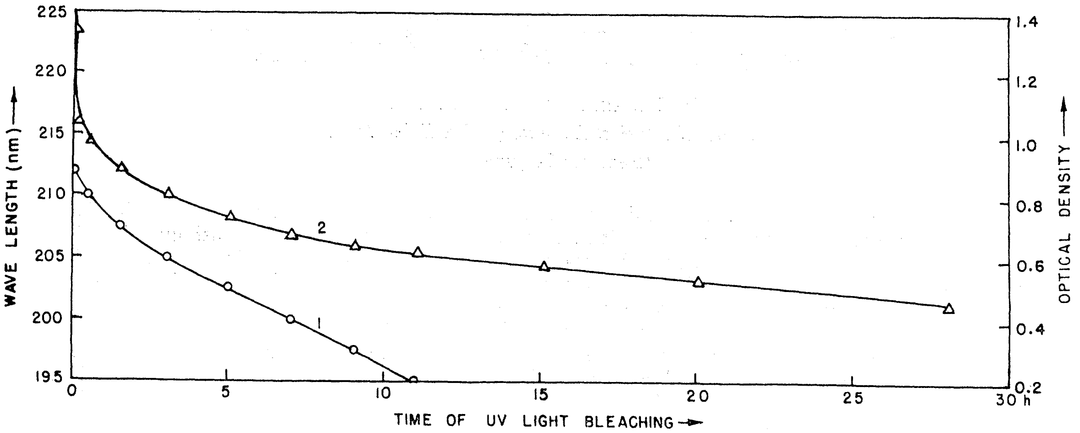

FIG. 1. Peak position (○) and optical density (△) as a function of the time of uv-light bleaching of x-irradiatively colored, highly pure KCl crystals. Curve 1 shows the peak position of the 212-nm band and curve 2 shows the optical density at the peak of the 230-nm band as a function of the time of uv-light bleaching.

(Atomic Energy Establishments, Trombay No. MR 125) and was in the range of ~300 R/per h. The slices were x irradiated from both sides (for about half of the time from each side) for uniform coloration.[10] Care was taken to avoid exposure of the crystal to stray light during the x irradiation and subsequent optical measurements.

The techniques of optical absorption measurements at RT and at higher temperatures and of thermal bleaching have been described earlier.[11]

For uv-light bleaching, the x-irradiated slices were kept at a position about 2 cm from the exit slit of the monochromator of the Hilger and Watt UVISPEK spectrophotometer, where the exit beam was sufficiently large to cover the x-rayed area of the slices. The width of the exit slit during the uv-light bleaching was kept at 1 mm. Maximum dispersion of the uv light in the region 195–230 nm with this slit width was ~0.5 nm.

3. RESULTS AND DISCUSSION

Highly Pure KCl Crystals

A slice 0.50 mm thick, cleaved from an H crystal was x irradiated at RT, in the dark, for 20 h. Two absorption bands in the uv region peaking at 212 and 230 nm were observed, in agreement with the results obtained by previous workers.[1] The absorption under the 212- and 230-nm bands is almost saturated in 20 h of x irradiation and the values of the optical density (OD) at the peaks of these two bands were 0.9 and 1.6, respectively. The x-irradiated slice was then subjected to uv-light bleaching. The positions of the absorption bands and the OD at the maxima of these two absorption bands were measured at regular intervals of times of uv-light bleaching. It was observed that the peak position of the 230-nm band remained unchanged, whereas that of the 212-nm band shifted continuously towards shorter wavelengths with the time of uv-light bleaching. The results are shown by curve 1 in Fig. 1. In 11 h of uv-light bleaching, the peak position of the 212-nm band shifts from 212 to 195 nm. The wavelength of the uv light (for bleaching the 212-nm band) was continuously changed to the value of the shifting peak position. With the present spectrophotometer the shift in peak position below 195 nm (when the x-irradiated slice was bleached with uv light for periods >11 h) could not be ascertained.

The OD at the shifting maxima of the 212-nm band remained practically unaltered up to 11 h of uv-light bleaching. For periods of uv-light bleaching >11 h, the OD, when measured at 195 nm, was observed to decrease. Presumably this long-term decrease in the 212-nm band when measured at 195 nm (for periods of uv-light bleaching >11 h) is due to a continuous shift of this band to shorter wavelengths and not due to an actual decrease in its optical absorption. Attempts made by bleaching the high-energy side of the 212-nm band did not reveal that it was a composite band.

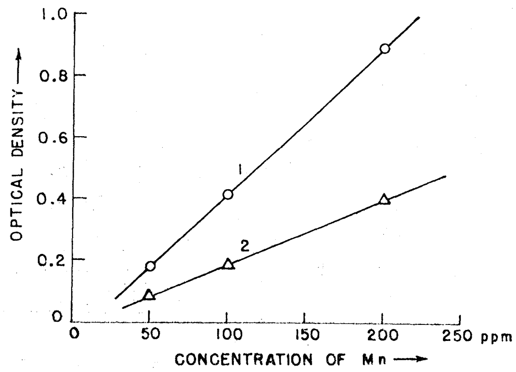

FIG. 2. Optical density as a function of the concentration of Mn in KCl:Mn crystals. Curves 1 (○) and 2(△) show the optical density at the maxima of the 201- and 273-nm bands, respectively.

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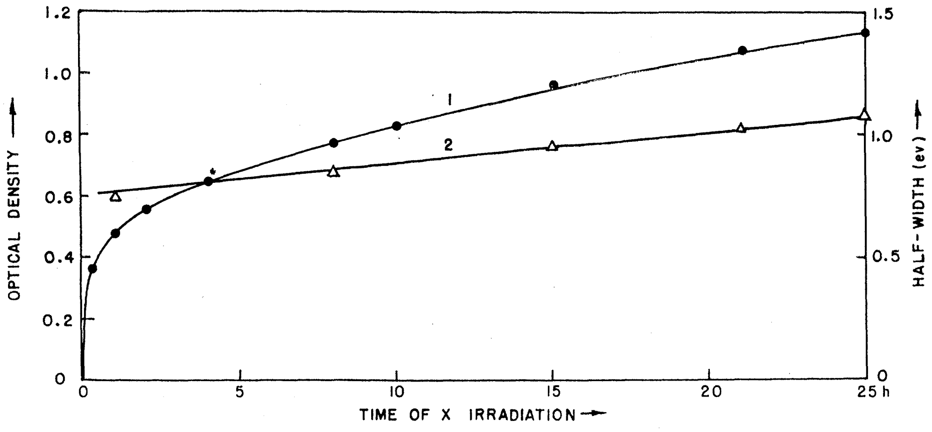

Fig. 3. Optical density (●) and half-width (△) as a function of the time of x irradiation in E3 crystal (containing 200 ppm of Mn). Curves 1 and 2 show, respectively, the optical density at the maximum of the 223-nm band and its half-width, as a function of the time of x irradiation.

However, if the optical absorption is measured at 212 nm while bleaching the crystal with uv light, the results obtained were similar to those of Zaleskiewicz and Christy.[7] In the case of the 230-nm absorption band, although the peak position remained unaltered, the OD at the maxima of this band decreased with the time of uv-light bleaching (curve 2 of Fig. 1). It is observed from curve 2 that the rate of bleaching of the centers responsible for the absorption at 230 nm is larger in the beginning (almost 50% of these centers bleach in the first 2 h) and very small thereafter (the other 50% of these centers bleach in about 25 h).

Another identical slice from the same H crystal was x irradiated, in the dark, for 20 h and the OD at the maxima of the 212- and 230-nm bands were 0.9 and 1.3, respectively. The x-irradiated slice was then heated in the dark at the rate of 5°C/min from RT to ~150°C. No change was observed either in the peak position or in the OD at the maximum of the 212-nm band. A slight decrease (~10%) of the OD at the 212-nm band (not shown in the figure) was observed when the slice was heated beyond 150°C (to ~200°C). The results that the 212-nm band does not bleach on heating the slice in the dark up to 150°C and that only a slight bleaching occurs when heated beyond 150°C (to ~200°C) are in qualitative agreement with the results of Zaleskiewicz and Christy.[7] However, a decrease in OD at the maximum of the 230-nm band, when the x-irradiated slice was heated at the rate of 5°C/min, was observed. On bleaching the slice thermally (results not shown), the decrease in OD at the peak of the 230-nm band was observed to be comparatively faster till ~120°C (OD decreased to almost 50% of its initial value); the rate of decrease of OD became rather slower thereafter (OD having decreased to about 20% when heated from 120 to 200°C). The peak position of the 230-nm band as in the case of uv-light bleaching remained unaltered during the thermal bleaching process also.

The shift in the peak position of the 212-nm band with the time of uv-light bleaching to lower wavelengths, and the absence of any such shift during the thermal treatment of the x-irradiated crystals, suggests that during the exposure to uv light some photochemical changes occur which perhaps alter the configuration or structure of the centers giving rise to the 212-nm band. The observation that there is practically no change in OD at the shifting maxima up to 11 h of uv-light bleaching and assuming that the oscillator strength of the newly formed centers remains unaltered, shows that the concentration of the newly formed centers remains unaffected during the uv-light bleaching. The observation that on thermal treatment the 212-nm band does not shift in its peak position and also that its OD decreases only slightly indicate that no such change takes place in the nature of these centers in the absence of the uv light and also that these centers are thermally stable.

Mn-Doped KCl Crystals

The optical absorption measurements made with crystals of KCl doped with different concentrations of Mn were reported earlier.[12] Two absorption bands in the uv region peaking at 201 and 273 nm, having half-widths of 0.36 and 0.15 eV, respectively, were observed. The intensity of these bands is found to increase with the concentration of Mn. Curves 1 and 2 of Fig. 2 show the increase in the OD at the peaks of 201- and 273-nm bands as a function of the concentration of Mn in these crystals. The observation that these uv bands appear on doping of the Mn impurity in pure KCl, and that the magnitude of these bands increases with the increase of the concentration of Mn, clearly shows that the presence of Mn in highly pure KCl crystals is responsible for these two uv bands.

Optical absorption measurements in the uv region of the x-irradiated slices cleaved from crystals E1, E2, and E3 were also made. The results obtained for different concentrations of Mn-doped crystals were qualitatively similar. Typical results obtained with crystal

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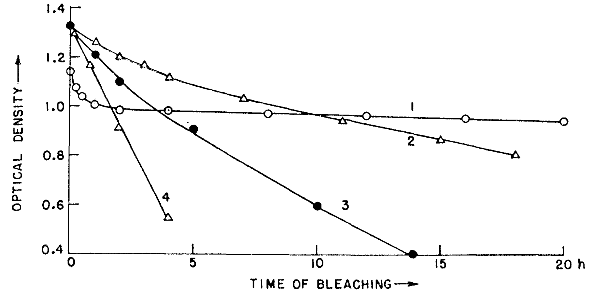

FIG. 4. Optical density as a function of the time of uv-light bleaching and thermal bleaching for an E3 crystal (containing 200 ppm of Mn). Curve 1 (○) is for a slice (x irradiated for 25 h) and bleached with uv light. Curves 2 (△), 3 (●), and 4(△) are for another three identical slices, each x irradiated for 28 h and bleached thermally in dark, at 50, 90, and 150°C, respectively.

E3 only are shown in Fig. 3. It was shown earlier[12] that on irradiation a new absorption band appears at 223 nm. Extensive studies were made on the growth of the OD at the maximum of the 223-nm band with the time of x irradiation; the results obtained are shown by curve 1 of Fig. 3. It was also observed that the OD at the peaks of the 201- and 273-nm bands and their half-widths, as a function of the time of x irradiation, remained unaltered. It is seen from curve 1 of Fig. 3 that the OD increases very fast in the beginning (the OD becomes 0.58 in the first two h of x irradiation) and the rate of increase of OD decreases thereafter (the increase in OD being from 0.58 to 1.15 in the next ~23 h). It was also observed that the half-width of the 223-nm band increased from 0.75 eV (for 1 h of x irradiation) to 1.10 eV for 25 h of x irradiation (curve 2 of Fig. 3). There was, however, no shift observed in the peak positions of the 201-, 223-, and 273-nm bands, with the time of x irradiation. The observation that the absorption bands peaking at 201 and 273 nm, on x irradiation, do not undergo any change either in their intensities, half-widths, or peak positions indicates that the centers responsible for these two bands are not at all affected in their configuration or interactions.

The centers giving rise to the 223-nm bands were also studied for their behavior towards optical and thermal bleaching. Four identical neighboring slices from crystal E3 were taken. One of the slices was x irradiated for 25 h and the OD observed at the peak of the 223-nm band was 1.15. The slice was then exposed, at RT, to uv light ($\lambda = 223$ nm). The OD at 223 nm was measured after regular intervals of time of uv-light bleaching. The effect of the time of uv-light bleaching on these centers is shown by curve 1 of Fig. 4. It is seen from this curve that there occurs only a slight initial decrease in the OD up to 2 h of uv-light bleaching and thereafter it remains practically unaffected. Each of the slices 2, 3, and 4 was x irradiated for 28 h and developed an OD = 1.3 at the peak of the 223-nm band. The thermal decay of the 223-nm band was studied in these slices by measuring the OD in slice 2 at 50°C, in slice 3 at 90°C, and in slice 4 at 150°C, as a function of time. Curves 2, 3, and 4 of Fig. 4 refer to slices 2, 3, and 4, respectively. It is seen from these curves that although the centers responsible for the 223-nm band are fairly resistant to optical bleaching, they are thermally unstable. From the results of thermal bleaching of the 223-nm band reported here and also from those obtained at other temperatures (results not shown), the activation energy $E_a = 0.54 \pm 0.02$ eV for the bleaching process was obtained.

It is now known[9] that certain divalent impurities in alkali-halide crystals give rise to new absorption bands in the uv region. From the observations of the increase in OD and the half-width with the time of x irradiation of the 223-nm band and the absence of any such band in the highly pure KCl crystals, the 223-nm band can probably be attributed to the presence of Mn impurity. From the data obtained regarding the band position, growth of OD, and of half-width, it can be concluded that the 223-nm band is perhaps a *D* band similar to the one observed by Ishii and Rolfe.[9] Further work, particularly in the behavior of the centers responsible for the 223-nm band to polarized light and EPR studies, may perhaps throw some light on the structure of these centers.

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