Effect of Simultaneous Optical Bleaching and Gamma Radiation on the Room-Temperature Colorability of KCl[†]

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The effect of simultaneous gamma irradiation and optical bleaching on F-center production in high-purity KCl at room temperature has been investigated. It is found that for high gamma-ray intensities ($\sim 4 \times 10^3$ R/min) simultaneous irradiation and bleaching decreases the net F-center production rate compared with that characteristic of the same samples irradiated in the dark. This suppression of F centers is associated with the later stage of coloration and is a function of bleaching intensity and dose rate. When a sample is given the same total dose and amount of bleaching *sequentially*, there is a small net decrease in the F-center concentration. However, this decrease is much less than the amount of suppression observed in crystals irradiated in light. The effect of simultaneous bleaching and irradiation on the late-stage coloration suggests that the charge state of the radiation-produced vacancies, e.g., whether F centers or α centers are formed, is very important in the coloration process. In the case of low dose rates (~ 92 R/min) the F-center growth curves in dark-irradiated crystals consist of essentially only early-stage centers, whereas in samples simultaneously bleached and irradiated (light-irradiated), F-center production was completely suppressed.

INTRODUCTION

IT is well established that room-temperature irradiation of alkali halide single crystals produces two general coloration stages which can be designated as early and late.[1,2] The production of F centers in both of these stages is dependent on radiation temperature, radiation intensity, and sample purity. The early or rapid stage of coloration is most pronounced for light irradiation doses or very low radiation intensities and is characterized by the relatively easy production of F centers. In fact, in this stage the energy required to produce a stable F center is very low, normally in the range of 600 eV.[2] Heavy irradiation at high intensities results in late-stage coloration for reasonably pure specimens and the energy expended per measurable F center in this coloration stage is between 2000 and 6000 eV, depending on the radiation temperature and intensity.[2]

Crawford and Nelson[3] have proposed that the easy F-center production in the early stage is due to the conversion of positive-ion vacancies, which are introduced with divalent impurities to maintain electrical charge neutrality, into negative-ion vacancies and subsequently into F centers by irradiation. The results of several recent experiments[4–6] on early-stage coloration tend to support this proposal.

Very little is known about late-stage coloration mechanisms, but investigations of the effect of impurities on the colorability suggest that electronic processes can be very important.[6,7] It was shown in previous work that only 0.3 to 0.5 ppm Pb impurity in KCl can suppress the late stage F-center colorability, at a given radiation temperature, intensity and dose, by approximately 25%.[7] The work of Härtel and Lüty[8] which showed that one particular charge state of the negative-ion vacancy is very mobile at room temperature suggests a mechanism through which electron-hole trapping could alter the net production of F centers. For example, electron trapping by impurities would reduce the concentration of electrons available to be trapped by negative-ion vacancies to make immobile F centers and could result in an increased concentration of mobile vacancies which would yield a greater number of aggregate color centers. It might be expected then, if electronic processes are important, that simultaneous optical bleaching and irradiation would change the F-center growth curves appreciably. Results from some preliminary experiments[9,10] already suggest that this might be the case. The purpose of this paper is to show

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TABLE I. Chemical analysis of impurities of Oak Ridge National Laboratory KCl boule No. 081463.

Impurity	Br	I	S	P	N	Na	Ca	Sr	Mg
Concentration (ppm)	19	<1	4	7	5	12	<2	<3	<1

that the optical pumping of electrons from F centers during irradiation can alter the F-center growth curves and, thus, to add more evidence that electronic processes do play an important role in the coloration processes.

EXPERIMENTAL PROCEDURE

The samples used in this investigation were all cleaved from a boule of KCl grown at the Oak Ridge National Laboratory. The results of chemical and spectrochemical impurity analyses, made at ORNL, are listed in Table I. The OH⁻ concentration as measured from the absorption band at 204 $m\mu$[11,12] was below 10^{16} centers per cm^3 and the carbon concentration less than 0.3%. The specimens used were 10×10 mm^2 in cross section and varied from 0.4 to 1.5 mm in thickness.

With one exception, a 200-Ci cobalt teletherapy unit was used for irradiation and the dose rate was varied from 92 R/min to 4×10^3 R/min by choosing different sample-to-source distances. One sample was irradiated in a homogeneous cobalt gamma field at a dose rate of 5×10^4 R/min.

The unfiltered beam from a Cenco illuminator (100-W tungsten lamp) was focused on the specimens for the bleaching experiments. To minimize radiation induced coloration of the illuminator lens, the light source was positioned at the side of the gamma shield with the light directed to a front surface mirror in the gamma beam which reflected the light onto the sample. A rigid stand was used to maintain the sample-mirror-illuminator geometry. The illuminator filament image formed on

the sample was slightly defocused to obtain uniform illumination. Photometric measurements made at the sample position indicated the bleaching light gave a flux for wavelengths in the F-band region of greater than $\sim 2 \times 10^{14}$ photons/cm^2 sec. The crystals were kept in complete darkness except during bleaching and optical measurements were made with a Beckman DK2 or Cary 14R spectrophotometer.

RESULTS

When two crystals cleaved from the same crystalline ingot are irradiated with low-intensity gamma rays (92 R/min), one in darkness and the other in white light, there is a marked difference in their colorability. This difference is depicted in Fig. 1, which is a plot of the absorption coefficient at the peak of the F band, α_F, versus the total gamma dose in roentgens. There was almost a complete suppression of the early-stage coloration in the sample that was optically bleached and irradiated simultaneously (dashed line); however, when the bleaching light was turned off and the radiation continued, the colorability of this specimen was very similar to that for the crystal irradiated in the dark (solid line). In fact, there was actually a "super" recovery with greater coloration than would have occurred if bleaching had not been done. In order to show that the bleaching light itself did not cause this change, the dark-irradiated specimen was bleached for a time equal to the radiation time and then replaced in the source and the radiation continued. It recovered, as can be seen in Fig. 1, to about the same coloration as was present before bleaching. In both crystals the M band was so small that it was not detectable with the apparatus used. This experiment was repeated using a sample of KCl: Ca with an early stage coloration height of about 2.5 ppm F centers as opposed to 0.4 ppm for
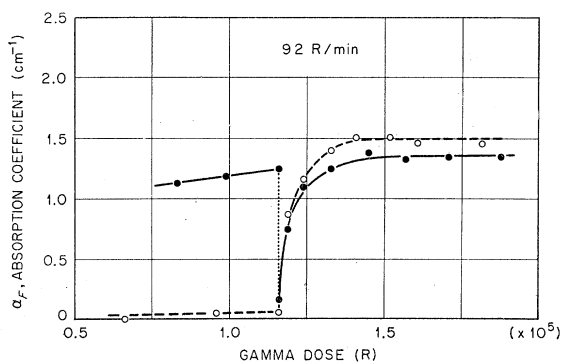

FIG. 1. F-center growth curves for Oak Ridge National Laboratory KCl irradiated at $\sim$92 R/min. ● Irradiated in dark. Sample bleached after $\sim 1.3 \times 10^5$ R and then irradiation continued in dark. ○ Simultaneous irradiation and bleach. After total dose of $\sim 1.3 \times 10^5$ R, irradiation continued in dark.
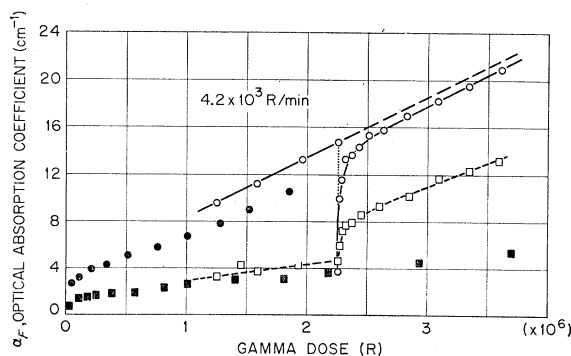

FIG. 2. F-center growth curves for Oak Ridge National Laboratory KCl irradiated at $\sim 4.2 \times 10^3$ R/min. ○ Sample irradiated in dark for 9 h. Sample bleached and then irradiation continued. ● Lowest F-center growth curve obtained with samples cleaved from Oak Ridge National Laboratory 081463 boule. □ Simultaneous irradiation and bleach. After 9 h irradiation, exposure was continued in dark. ■ Simultaneous irradiation and bleach. These data indicate approximate sample variation and reproducibility of the data.

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the early stage of "pure" crystals. Simultaneous bleaching and irradiation again resulted in almost complete suppression of the coloration, but "super recovery" for a light-irradiated and then dark-irradiated Ca-doped specimen was not detected.

The effect of simultaneous bleaching and irradiation on the late stage coloration is shown in Figs. 2 and 3. These figures are similar to Fig. 1 but extend to much greater gamma-ray doses (the abscissa is now in millions of roentgens). The radiation intensity in this case was 4×10^3 R/min, much higher than before. When a sample is irradiated for 9 h to a gamma dose of about 2.2×10^6 R so that the coloration is well into the late stage, it is possible to separate late-stage coloration processes from those of the early stage. It is evident from the figures that the result of the bleaching treatment for late-stage coloration is much different from that for the early stage. There is a suppression of the coloration for the "lights on" sample just as there was for the early stage; but more significant is the fact that when the irradiation is continued with the specimen in the dark, the recovery of the coloration to the curve characteristic of the "lights off" sample is not complete. There is a net suppression of late-stage F centers due to optical bleaching during radiation. In order to show that just bleaching a sample for 9 h is not sufficient to cause this result the "lights off" sample was bleached for 9 h and then re-irradiated. When a sample is irradiated in the dark then optically bleached and then re-irradiated in the dark, there is always an apparent slight decrease in the F-center growth curve. However, this decrease is always much less than that caused by simultaneous bleaching and irradiation. It should also be noted that the early-stage coloration is not completely suppressed by the bleaching when rather high-intensity gamma irradiation is used.
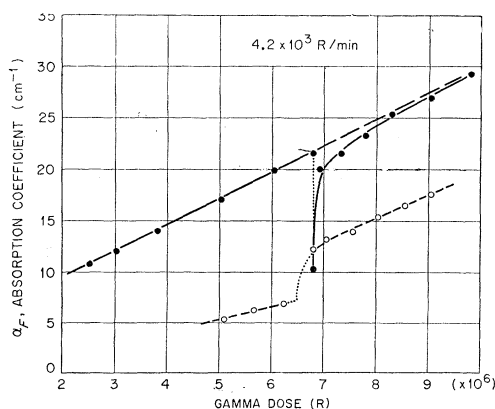
DISCUSSION

Figure 1 shows that optical bleaching during low-intensity irradiation can result in almost complete suppression of the early-stage colorability. The amount of early-stage coloration that can be suppressed is dependent, however, on the intensity of the bleaching light and the intensity of the radiation source. This can be seen by comparing the early-stage coloration heights for the "lights on" crystals in Figs. 1 and 2 where different irradiation intensities were used. Covault and Pearlstein[9] have made similar observations on the early-stage coloration and they also found a "super" recovery very much like that shown in Fig. 1 for some of their specimens when the bleaching light was extinguished and the irradiation continued in the dark. Their results indicate that the early-stage effects are very sample-dependent. This might be expected, since this coloration stage is so sensitive to dislocation content, and impurity type. It is difficult, for this reason, to make many definitive remarks about the early-stage effect and our interest will be primarily centered on the effect of simultaneously bleaching and irradiation on the late-stage coloration.

Since we were particularly interested in late-stage colorability, it was necessary to show that the total concentration of early-stage F centers was less than that for late-stage centers in the heavily irradiated crystals. The concentration of early-stage F centers is intensity dependent[6]; more are formed at high-intensity irradiation than at low intensity. Therefore, a rough estimate of the total concentration of early-stage centers that can be produced in a particular sample can be obtained by a high-intensity radiation. Figure 4 is a plot of the F-band absorption coefficient versus the radiation dose for a sample irradiated at a high-intensity (5×10^4 R/min) which yields a large early stage. The figure shows that the early-stage coloration has saturated at an absorption coefficient of about 5 cm^{-1}.
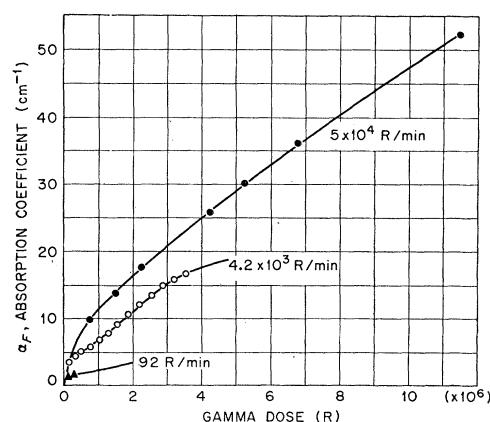
Fig. 3. F-center growth curves for Oak Ridge National Laboratory KCl irradiated at $\sim4.2\times10^3$ R/min. ● Sample irradiated in dark for ~21 h. Sample bleached and then irradiation continued. ○ Simultaneous irradiation and bleach. After ~20 h irradiation was continued in dark.

Fig. 4. F-center growth curves for Oak Ridge National Laboratory KCl. ▲ 92 R/min, ○ 4.2×10^3 R/min and ● 5×10^4 R/min. The 5×10^4 R/min data were obtained with samples irradiated in a homogeneous gamma flux field at Oak Ridge.

Thus, as is illustrated in Figs. 2 and 3, the coloration was well past the early-stage range before we made any changes in experimental conditions. When a crystal is dark-irradiated into the late stage, we find that optical bleaching results in a net loss of around 5–10% of the F centers. This loss can be detected by a short re-irradiation in the dark which destroys F-aggregate centers formed by the bleaching and regenerates the F band.[13] Figures 2 and 3 show clearly that there is a small net loss in F centers after bleaching and re-irradiation. This result is in agreement with flow-stress measurements on irradiated KCl where it was found that extensive bleaching decreased the flow stress of an irradiated sample by about this amount.[14] The more important observation is that bleaching during irradiation suppresses the colorability by as much as 30%. This is further evidence that electronic processes are very significant in the coloration mechanism. Measurements of the influence of trace impurities on the colorability have lead to this same conclusion. Electronic processes can suppress the coloration in a number of ways, and we will briefly outline one of these. It is known that an F-type defect (either the excited F center, α center or F' center) becomes mobile under irradiation or optical bleaching,[8,13] whereas in the dark there is no migration of F centers. If we assume that the alpha center is the mobile entity, then it is understandable that a very efficient electron trap which reduces the net concentration of electrons available to be trapped by negative-ion vacancies would enhance the concentration of mobile alpha centers. These mobile alpha centers could then move around and be annihilated or form F-aggregate centers reducing the net F-center coloration. Similarly optical bleaching during irradiation would increase the number of alpha centers relative to F centers leading again to a net reduction of F coloration. Therefore optical bleaching during irradiation and the trapping of electrons by vacancies, impurities, and dislocations can play a major role in the net production of F centers. Furthermore, there is now reasonable evidence[14,15] that interstitials are produced simultaneously with negative-ion vacancies during irradiation at room temperature and it could be that the mobility of the interstitial is also dependent on its charge state.

Under the general category of electronic processes there are several possible explanations for the suppression of the coloration by optical bleaching during irradiation. Optical bleaching during irradiation will cause more mobile vacancy centers to be present and thus result in the formation of more F aggregates. Perhaps some of these aggregate centers are not destroyed on re-irradiation with the bleaching light off. In view of previous experiments which show a radiation equilibrium between F centers and F aggregates this is not very likely.[16,17] There is the possibility that vacancy-interstitial recombination may be greatly enhanced or reduced by the charge state of either the vacancy or the interstitial, or the mobility of either the interstitial or an F entity may be increased so that recombination becomes more likely. In fact, there are some results[18,19] which suggest that vacancy-interstitial recombination may be inhibited by interstitial clustering during irradiation at room temperature. If this is the case, then the mobility of vacancies and interstitials is extremely important, and if an F entity is very mobile it should be able to annihilate interstitials before clusters can be formed. This would result in a net loss of F centers. In summary, we believe that the data presented add further evidence that electronic processes affect the recombination rate of vacancies and interstitials and that a more detailed study of the bleaching effect during irradiation on crystals containing known concentrations of certain impurities should help to clarify their role in the coloration processes.

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Erratum

Specific Heats of Copper, Silver, and Gold below 30°K. Douglas L. Martin [Phys. Rev. **141**, 576 (1966)]. On p. 579, column 2, line 5, 20.368°K should be 20.378°K.