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Studies on F-band absorption of irradiated KCl single crystals excited with laser light

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The absorption in the F-band of KCl single crystals after X-ray irradiation and subsequent excitation with laser light is studied. Similar investigations have been carried out when these crystals are subjected to high a.c. electric fields prior to X-ray irradiation and also at elevated temperatures. The effect of laser excitation on γ-ray irradiated samples is studied. An attempt is made to interpret the results in terms of the disorder that sets-in in these crystals.

1. Introduction

The colour centre phenomenon in alkali halide crystals has been extensively studied and has paved the way for considerable insight into the defect processes taking place in them [1–3]. The influence of plastic deformation on the colour centre phenomenon in alkali halides is to enhance the F-centre yield [4]. If alkali halide crystals are subjected to an appreciable fraction of their electrical breakdown strength ($\approx 10^6$ V) and subsequently irradiated with X-rays, a significant increase in F-centre concentration is observed [5, 6]. It has been shown [7, 8] that a considerable concentration of F-centres is destroyed even at room temperature ($\approx 30°$ C) by subjecting X-ray irradiated alkali halide crystals to high a.c. or d.c. electric fields. A similar decrease in F-centre concentration was observed in X-ray irradiated KCl and NaCl crystals when they were subsequently excited with laser light [9, 10]. A study of the influence of laser excitation on X-ray irradiated alkali halide crystals through controlled variation of defect concentration can yield valuable information in understanding the processes leading to the decrease in F-centre concentration in such crystals. It is the aim of this paper to report the results of such studies in KCl single crystals.

2. Experimental methods

The KCl crystals used in the present work are laboratory grown; measurements were also taken on samples obtained as a gift from the Crystal Physics Laboratory, Massachusetts Institute of Technology, USA. The samples were cleaved and polished, the final dimensions being 1 cm × 1 cm × 0.1 cm. Apparatus having a step-up transformer with proper ratings and a laboratory-made sample holder were used for a.c. field treatment.

X-ray irradiation was performed at room temperature ($\approx 30°$ C) for 1 h (unless otherwise stated), with 35 kV and 10 mA, keeping the samples 2 cm away from the window of a Norelco Unit. γ-ray irradiation was carried out with a ^{60}Co source of 10^3 Ci strength giving out a dose of 78 k rad h^{-1}, for 54 h. Excitation with laser light by a He–Ne laser, 2 mW power and 632.8 nm wavelength was undertaken, keeping the samples at a distance of 30 cm from the laser.

The F-band absorption measurements were taken using a Beckman 26 Spectrophotometer at room temperature. The accuracy in the measurement of the absorption coefficient (α cm^{-1}) was 0.03.

3. Results

The F-band absorption characteristic of X-ray irradiated KCl crystals showed an absorption peak at 560 nm. F-band absorption is found to decrease with the time of laser excitation (i.e. laser dose). Using Smakula's equation and assuming the F-band to be guassian in shape, the F-centre concentration in these samples under various conditions is calculated and plotted as a function of time of laser excitation. Fig. 1 shows the F-centre concentration for KCl crystals which have been initially subjected to various high a.c. electric fields, then X-ray irradiated and subsequently excited with laser light. The F-centre concentraton in these samples was found to decrease with time of laser excitation and this decrease was in two stages. The initial F-centre concentration in the field-treated samples was observed to be larger compared to as-cleaved and X-ray irradiated samples; also the initial F-centre concentration increased with increasing magnitude of a.c. field. The decrease in F-centre concentration with time of laser excitation was found to be larger and faster in KCl samples which were subjected to higher a.c. electric fields.

Fig. 2 shows the concentration of F-centres in γ-ray irradiated KCl samples subsequently excited with laser light for various times. Here also we found a two-stage decrease in the F-centre concentration with laser excitation. This figure also gives F-centre concentration in X-ray irradiated KCl crystals (X-ray irradiated for $\frac{1}{2}$ h when the F-centre concentration is practically the same as in the γ-ray irradiated samples) which were later excited with laser light. It can be seen

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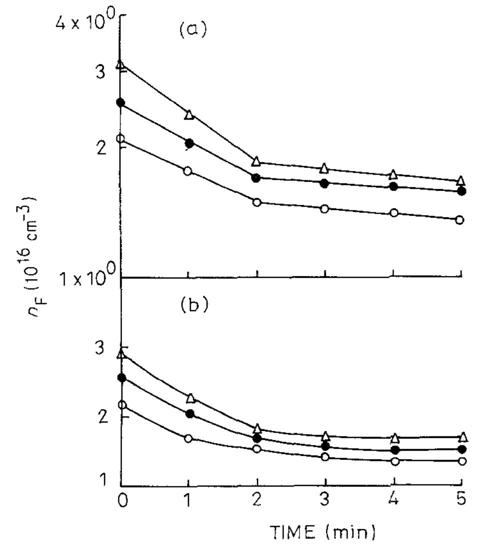

Figure 1 Change in F-centre concentration of a.c. field treated, X-ray irradiated KCl crystals later excited with laser light on (a) an ordinary scale, (b) a semi-log scale. (○) 0 V cm^{-1}, (●) 40kV cm^{-1}, (△) 60 kV cm^{-1}.

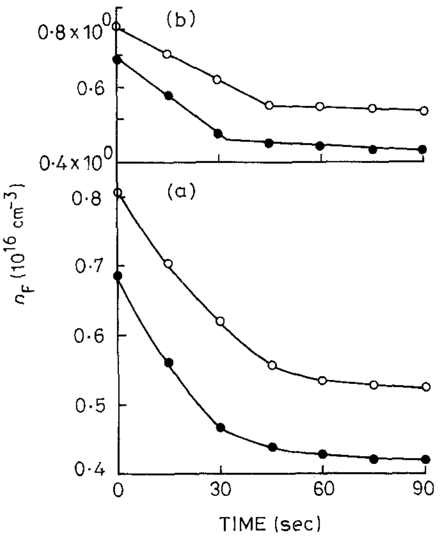

Figure 3 Change in F-centre concentration with time of laser excitation for KCl crystals which are X-ray irradiated and later excited with laser light at elevated temperatures on (a) an ordinary scale, (b) semi-log scale. (○) 70° C, (●) 115° C.

from this graph that the decrease in F-centre concentration in γ-ray irradiated samples was smaller and slower compared to X-ray irradiated samples for the same laser excitation times.

F-centre concentration as a function of laser excitation for KCl crystals which were X-ray irradiated at different temperatures and excited with laser light at that temperature, is shown in Fig. 3. We noticed that the initial concentration of F-centres in these crystals was smaller compared to that when these were irradiated at room temperature. Subsequent laser excitation of these irradiated samples decreased the F-centre concentration at a faster rate and more efficiently.

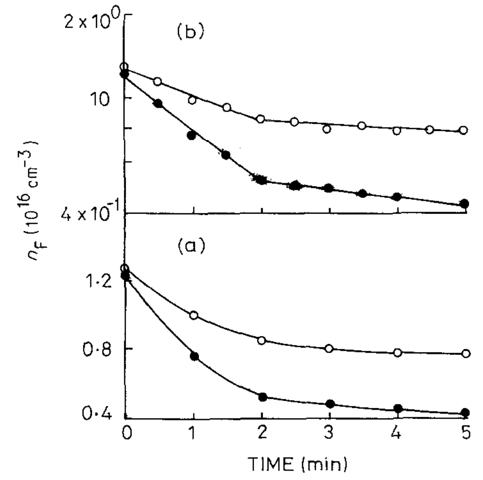

Figure 2 Change in F-centre concentration as a function of time of laser excitation for (●) X-ray irradiated or (○) γ-ray irradiated KCl crystals on (a) an ordinary scale, (b) a semi-log scale.

4. Discussion

If the irradiated alkali halide are excited with laser light a considerable interaction of laser light with the crystal lattice can occur, particularly in the major defect regions like dislocations, leading to a considerable increase in the disorder already produced due to irradiation. This increased disorder seems to facilitate the destruction of F-centres even at room temperature [9, 10]. It seems reasonable to assume that the disorder created by laser excitation would be larger in the regions where initially dislocations and vacancy clusters are present in the crystal (compared to the normal lattice regions). Therefore, we expect a larger and faster decrease in F-centre concentration with time of laser excitation in these perturbed regions of the crystal lattice (Stage I). The disorder in the vicinity of F-centres formed in the normal lattice of the crystal is comparatively less and we can ascribe a slower F-centre reduction rate for this region (Stage II). Also, the rate of decrease of F-centre concentration would be proportional to the concentration of F-centres present, and because F-centres normally tend to accumulate around major defect regions, the decrease in F-centre concentration in Stage I would be larger than that in Stage II. For the Stages I and II we can write

$$\frac{dN_p}{N_p} = -K_1\,dt \qquad (1)$$

and

$$\frac{dN_n}{N_n} = -K_2\,dt \qquad (2)$$

where N_p is the concentration of F-centres in the perturbed regions of the lattice and N_n is concentration in the normal regions, K_1 and K_2 are proportionality constants. By integration of the above equations, we get

$$N_p = n_1 e^{-K_1 t} \qquad (3)$$

and

$$N_n = n_2 e^{-K_2 t} \qquad (4)$$

where t is the time of laser excitation. The total number of F-centres, N, would then be

$$N = N_p + N_n = n_1 e^{-K_1 t} + n_2 e^{-K_2 t} \qquad (5)$$

where n_1 is the initial concentration of F-centres and n_2 relates to the possible initial number of F-centres that

TABLE I Values of K_1 and K_2 in KCl crystals X-ray irradiated and subsequently laser excited at different elevated temperatures

X-ray irradiation temperature (° C)	K_1	K_2
30	0.27×10^{16}	0.06×10^{16}
70	0.52×10^{16}	0.04×10^{16}
115	0.75×10^{16}	0.10×10^{16}

could have been present in the crystal if the lattice was free from dislocations and vacancy clusters. The values of K_1 and K_2 for as-cleaved KCl crystals, X-ray irradiated for 1 h and later excited with laser light are 0.27×10^{16} and $0.06 \times 10^{16}\,\text{min}^{-1}$, respectively. It is known that vacancies are produced in alkali halide crystals when they are subjected to high a.c. electric fields [11] leading to a concentration of F-centres in them on subsequent irradiation and hence larger initial disorder being present in the crystal. Therefore, values of K_1 and K_2 and a decrease in F-centre concentration are expected to be larger in a.c.-field treated samples.

Our measurements on γ-ray irradiated and subsequently laser-excited samples indicate a slower and smaller decrease in F-centre concentration compared to the X-ray irradiated and laser-excited samples even though the initial concentration in both γ-ray and X-ray irradiated samples is the same. The rates of destruction of F-centres (values of K_1 and K_2) for X-ray irradiated samples were found to be larger than those of γ-ray irradiated samples (Table I). These different rates of decrease in the F-centre concentration can be understood by looking at the details of the creation of F-centres during X-ray or γ-ray irradiation [3]. We know that in X-ray irradiated crystals, the effect of irradiation decreases exponentially from the surface of the crystals. Hence in such crystals, coloration is practically a surface effect where all the colour centres are concentrated on the surface layers of the crystal; therefore, in X-ray irradiated crystals, disorder due to irradiation is more restricted to the surface. However, γ-ray irradiation produces a bulk effect where the formation of F-centres and other defects (and consequent disorder) is uniformly distributed throughout the bulk of the crystal. The present results showing a larger decrease in F-centre concentration in X-ray irradiated crystals, when they are laser excited, compared to γ-ray irradiated samples (the initial concentration of F-centres being the same in both cases) seems to suggest that the total disorder on the surface in X-ray irradiated samples is greater than that in γ-ray irradiated ones.

Excitation with laser light at an elevated temperature of the samples X-ray irradiated at the same elevated temperature is found to affect the bleaching rate in Stage I considerably. The destruction of F-centres under the influence of laser light can occur in two different ways. Direct recombination of F-centres with hole-trapped centres or interstitials can take place because of the disorder created in the lattice [9, 10]. Ionization of defect centres resulting from lattice distortion, particularly in the major defect regions, would lead to the destruction of F-centres. The ionic process which requires the motion of F^+-centres and other defects like vacancies, will generally lead to the formation of more complex defect centres like M-centres, R-centres, etc. [2]. Also an increase in temperature of the crystals increases their thermal energy, resulting in an increased amplitude of vibration of atoms or ions. Under these conditions, if the crystals are excited with laser light the electrons and holes trapped in electron centres and hole centres may recombine because of the increased disorder. The larger destruction rates for the crystals which are irradiated at elevated temperatures and subsequently laser excited at that temperature, seems to support these ideas. Also it is found that there is some decrease in the absorption of M-bands in these crystals [9, 10]. X-ray irradiation and laser excitation increased the concentration of vacancies in these crystals [11, 12]. The destruction of F-centres is observed to be a radiative process with the emission of light [13]. All these observations, together with the present results suggest that the decrease in the F-centre concentration is because of direct recombination of electrons and holes.

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