# Formation and stabilization of F centres in a KBr crystal induced by $N_2$ laser light irradiation at room temperature

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# Formation and stabilization of F centres in a KBr crystal induced by $N_2$ laser light irradiation at room temperature

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**Abstract.** The relationship between the power of the $N_2$ laser light focused on a KBr crystal and the concentration of resultant F centres produced in the crystal has been examined at room temperature using a He–Ne laser light as the probe light. The observed linear relationship existing between them has been interpreted by considering the rate equation for F centre formation. It has been found that the F centres produced under repeated irradiation of the laser light are thermally very stable. Therefore, possibility of application to a colour-centre laser is presented.

## 1. Introduction

There are many different kinds of method for producing colour centres in alkali-halide crystals. Of these, additive colouration, electrolytic colouration and x-ray irradiation are known as conventional methods (Schulman and Compton 1963). However, the two-quantum photoionization technique using a high-power pulsed laser is most novel and attractive. In this case colouration is achieved very easily in a short time without any special treatment, only by focusing the laser light onto the crystal. Other advantages of this method are that the colour centres induced are distributed uniformly in the crystal, and these colour centres are thermally stable compared with those produced by x-ray irradiation and electron beam irradiation.

Gellar *et al* (1967) proved for the first time that F centres are produced in a KBr crystal when high-power $N_2$ laser light was focused onto the crystal at room temperature. Kagawa and Nakaya (1975) and Kagawa (1976) made transient observations on the absorption spectrum of the F centre and trapped-hole centres induced in a KBr crystal at liquid-nitrogen temperature. On the basis of the experimental results, the mechanism for forming the F centres was discussed in comparison with those for the formation of F centres by electron beam irradiation or x-ray irradiation (Kagawa 1976). Similar experiments were made at a further lower temperature of around 10 K by the group at Kyoto University (Kan'no *et al* 1980, Itoh *et al* 1981). A detailed study of the dynamical process of F-centre formation has been achieved by the Naval Research Group (Bradford *et al* 1975, Williams 1976) and by the groups at Tohoku University (Suzuki *et al* 1979, Hirai *et al* 1987) using various kinds of picosecond laser. However, no report has been given of the relationship between the intensity of the laser light and the concentration of the colour centres induced. In this paper, we report the $N_2$ laser power dependence against the content of F centres induced in the crystal, and the stabilization of the F centres when the crystal is repeatedly irradiated

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with laser light. This stabilization technique is very important when we try to employ laser-induced colour centres for colour-centre lasers.

## 2. Experimental procedure

The experimental arrangement is shown in figure 1. The $N_2$ laser used in this study was a high-power coherent TE $N_2$ laser using a four-stage oscillator–amplifier system, which was designed and constructed in our laboratory (Kagawa *et al* 1988). The characteristics of the laser light obtained from the laser system are as follows; a maximum power of 1.3 MW, a pulse width of 6 ns and a beam divergence of less than 1 mrad with a beam cross section of 10 mm × 20 mm at the exit window of the laser. The laser pulse energy was changed by inserting glass plates as attenuators and the pulse energy was detected with a joule meter (Gentec ED-200). Except for the experiment with single-shot irradiation, the laser was operated with a repetition frequency of 5 Hz, and the irradiation time interval was changed using optical shutter 1. The laser light was focused inside the crystal by a fused quartz lens $L_1$ ($f = 70$ mm).

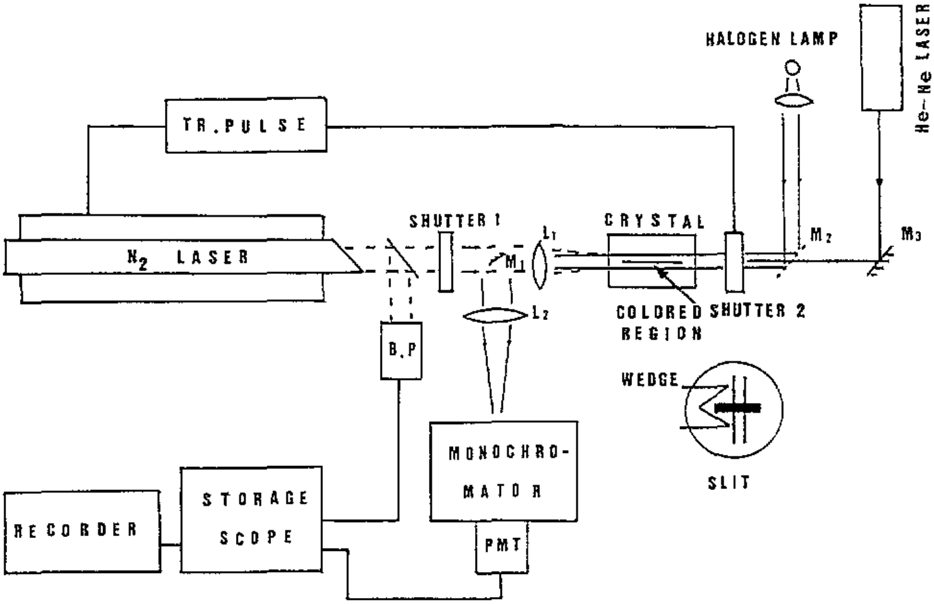

**Figure 1.** Schematic diagram of the experimental set-up.

In order to observe the absorption due to colour centres, which are filamentarily distributed (cross section, about 0.5 mm×0.1 mm) along the path of the laser light, the image of the coloured portion was enlarged and projected on the entrance slit of a monochromator (Nikon P-250) with the aid of two lenses $L_1$ and $L_2$ ($f = 500$ mm), and a small mirror $M_1$. When use is made of a wedge in front of the entrance slit, only the part of the probe light that had passed through the coloured portion was allowed to enter the spectroscope. A He–Ne laser (1 mW) in combination with a filter was used as a probe light for observing the change in the absorbance at the F band. When the absorption spectrum was taken, the light from a halogen lamp (6 V; 20 W) was used, and the wavelength of the monochromator was scanned in the range from 500 to 720 nm with a speed of 135 nm $\mathrm{min}^{-1}$ after the laser pulse irradiation.

The optical signal from a photomultiplier (Hamamatsu R-1104) was stored in two-channel digital oscilloscope (Kikousui 2050 A). When the transient change in the absorbance due to single-shot laser irradiation was observed, the laser oscillation was synchronized with optical shutter 2. Specimens of nominally pure KBr crystal were obtained from Harshaw Chemical Co., and another crystal was obtained from Horiba Co., Japan. The crystal dimensions used in this work were about 20 mm × 10 mm × 10 mm. All measurements were made at virgin positions by moving the crystal with micrometer screws after the laser pulse irradiation.

## 3. Results and discussion

Figure 2 shows the relationship between the power of the $N_2$ laser and the optical density of the F absorption band. This experiment was made with single-shot laser irradiation. It is clearly seen that the concentration of F centres induced in the crystal is not proportional to the square of the intensity of the laser light but is linear, in spite of the fact that the colouration takes place through a two-photon absorption process of the laser light. Also it should be noted that, in the case of the Harshaw crystal, saturation is observed in the range of high powers of the laser light. These results are interpreted qualitatively by considering the rate equation for the F-centre formation as follows:

$$\mathrm{d}n/\mathrm{d}t = aI^2 - bIn - cI^2n \tag{1}$$

where $n$ is the concentration of F centres at time $t$ after the initiation of the laser pulse irradiation, $I$ is the laser light intensity at time $t$, and $a$, $b$ and $c$ are the coefficients of each term. The first term on the right-hand side of equation (1) shows that F centres are produced by two-photon absorption of the laser light. The term $bIn$ represents the loss process in which the F centres once produced are optically bleached by absorbing the laser light, because the wavelength (337.1 nm) of the laser light coincides with the tail of the $L_2$ absorption band, which is one of the higher excited states of F centres (Schulman and Compton 1963). The term $cI^2n$ also represents the loss process in which the F centres once produced recombine with Br atoms travelling through the crystal in the form of a replacement sequence (Itoh and Saido 1973); according to the excitonic model, the Br atoms are pushed out of the self-trapped excitons when F centres are formed (Pooley 1966).

Let the pulse of the laser light be of a square form with a duration of $t'$. Then we can solve equation (1) easily with the initial condition $n = 0$ at $t = 0$:

$$n = aI\{1 - \exp[-(bI + cI^2)t']\}/(b + cI). \tag{2}$$

If we assume that $bI + cI^2 \gg 1$, we have

$$n = aI/(b + cI). \tag{3}$$

From this equation, it is clearly shown that

$$n \simeq (a/b)I \qquad b/c \gg I \tag{4}$$

$$n \simeq a/c \qquad b/c \ll I. \tag{5}$$

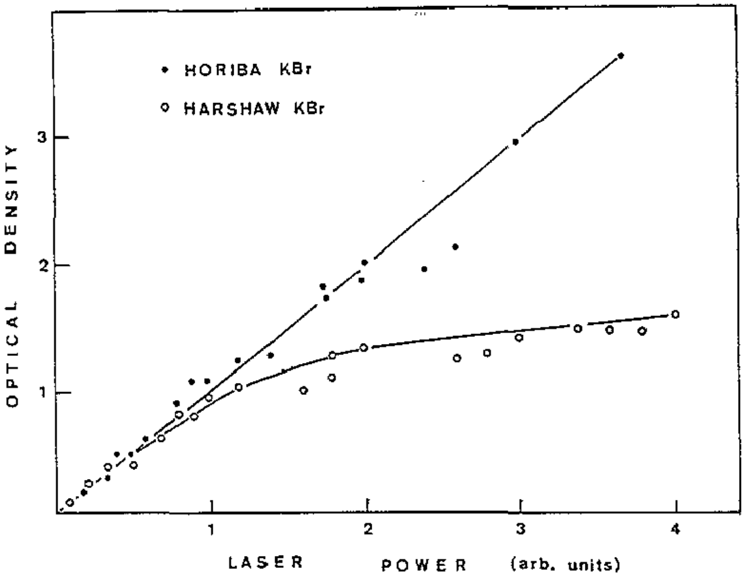

**Figure 2.** Relationship between the power of the $N_2$ laser and the optical density in the F absorption band.

The experimental curve observed in the case of the Harshaw crystal can be interpreted well using equations (4) and (5).

In the case of the Horiba crystal, rather high concentrations of impurities such as $Na^+$ and $Ca^{2+}$ are assumed to be present. In this case, the probability that Br atoms encounter impurities to form $V_1$ trapped centres becomes high during the replacement sequence process. As a result, the probability of recombination between Br atoms and F centres would be reduced. Therefore, it is supposed that the relation $b/I \gg c$ still holds even in the range of high powers of the laser light. This explains the experimental curve for the Horiba crystal.

When the crystal initially contains F centres at a concentration of $n_0$, the change $\Delta n$ in the concentration of F centres induced by the next laser pulse with a power intensity $I'$ $(I' < I)$ is

$$\Delta n = aI'/(b + cI') - n_0. \tag{6}$$

In this case, the assumption that $bI' + cI'^2 \gg 1$ was used. Furthermore, under the condition $b/c \gg I'$, equation (6) can be expressed as follows:

$$\Delta n = aI'/b - n_0. \tag{7}$$

As shown in equation (7), the sign of $\Delta n$ changes depending on the balance between $n_0$ and $aI'/b$. That is, $\Delta n$ possibly becomes negative when $aI'/b$ is smaller than $n_0$. This was confirmed experimentally. For this purpose the Horiba crystal which contains a large amount of F centres owing to repeated irradiation of the laser light was employed. Using the crystal it was demonstrated that the transparency of the crystal increased reversely and did not decrease, when the next laser pulse was irradiated with reduced pulse energy compared with that of the previous irradiation.

Figure 3 shows the feature of thermal bleaching of the F centres after the repeated irradiation of the laser light at the same position in the Harshaw crystal. In this experiment, the power of the laser light focused onto the crystal was fixed at 2 mJ. An experiment using the Horiba crystal was also made. The result showed similar features, but thermal stabilization was inferior to that for the Harshaw crystal.

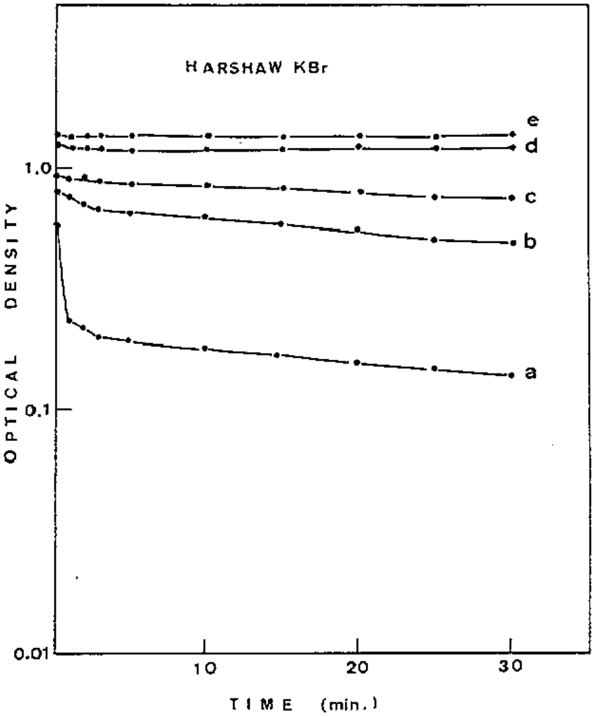

**Figure 3.** Thermal bleaching of F centres in a KBr crystal after the $N_2$ laser pulse irradiation with various numbers of shots: curve a, one shot; curve b, five shots; curve c, 15 shots; curve d, 50 shots; curve e, 150 shots. The samples used for the thermal bleaching studies were kept in darkness.

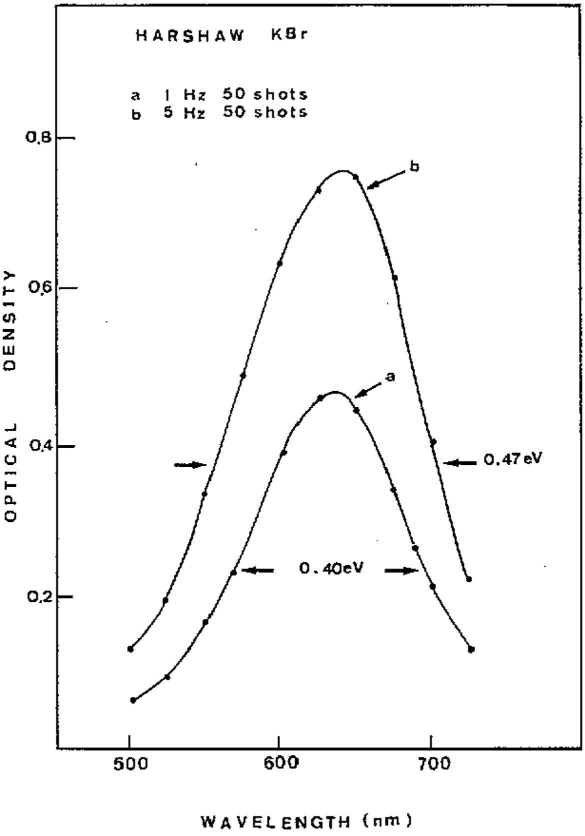

**Figure 4.** Comparison of the absorption spectra obtained in two irradiation cases: curve a, 1 Hz irradiation; curve b, 5 Hz irradiation. The number of total irradiation shots was the same, namely 50, in each case.

As shown in figure 3, in the case of single-shot irradiation, the qualitative feature of the bleaching is that it occurs relatively rapidly at first and then becomes difficult. As we have already described in a previous paper the F centres produced by irradiation with $N_2$ laser light are very stable compared with those produced by other ionizing radiation such as x-rays and an electron beam. This has been interpreted in terms of a model in which the replacement sequence under the $N_2$ laser light irradiation is forced to travel a long distance, because F-centre formation under $N_2$ laser light irradiation comes from the $(V_K^* + e)$ state, where $V_K^*$ is the excited $V_K$ centre produced by absorption of a single photon of $N_2$ laser light (Kagawa 1976).

Furthermore, the experimental result shown in figure 3 is very interesting because with increasing number of shots of laser pulse the share of the fast-decay component decreases and the decay time of the slow component also becomes longer. It was observed that, in the case of 150-shot irradiation, only a few per cent of F centres were thermally bleached in 2 h when the crystal was kept in darkness.

It should also be emphasized that, if the irradiation was undertaken at 1 Hz repetition frequency but with the same total number of shots, the resultant optical density of the F band decreased to a considerable extent compared with the case for 5 Hz irradiation, and the degree of stabilization of the F centres decreased. Figure 4 shows the comparison of the absorption spectra obtained in the two irradiation cases: curve a is for 1 Hz irradiation and curve b for 5 Hz irradiation. In this experiment the number of total irradiation shots was kept at 50. It is noted that the half-width of the F band for 5 Hz irradiation is as large as 0.47 eV, while in the case of 1 Hz the width is almost the same as that of the ordinary F band at room temperature (0.4 eV). The concentration of F centres for 5 Hz irradiation was estimated to be about $4 \times 10^{15}$ cm$^{-3}$ using the Sumakura equation (Schulman and Compton 1963). This wide F band suggests either that there is superposed absorption due to different species or that the F centres are perturbed by some nearby associated defects.

Although further study is required, we propose a model in which, in the case of repeated irradiation with $N_2$ laser light, V centres once produced are excited by absorbing one photon of laser light and some unknown reaction takes place in the crystal, forming other different kinds of trapped-hole centres which are expected to have a higher activation energy and be thermally more stable.

Our final goal of this study is not only to elucidate the mechanism occurring in the crystal due to $N_2$ laser light irradiation but also to realize new colour-centre lasers using this colouration method. A detailed study on this subject will be reported elsewhere in the near future.

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