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Photoionization processes in F aggregate centres of LiF crystal

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Abstract. Extensive studies have been carried out on the optical conversion of F and F-aggregate colour centres produced in lithium fluoride single crystal on gamma irradiation. Using 308 nm XeCl laser it has been shown that significantly large population build-up of F_3^+ centre and reduction in the population of undesirable F_2 centres can be achieved in gamma irradiated crystal at room temperature due to multistep photoionization processes. These and other investigations have provided a scheme for possible laser action based on F_3^+ colour centres in LiF crystal at room temperature.

Keywords. Photoionization; lithium fluoride; F aggregate centres; XeCl laser; colour centre laser.

PACS Nos 42·55; 81·40; 78·50

1. Introduction

Various types of colour centres such as F and F-aggregate centres are produced in alkali halides on gamma irradiation with large doses at room temperature; however, amongst them the population of F-aggregate centres is quite low [1]. Optical and thermal bleaching behaviour of F centres in various alkali halides has been well investigated [2–4] from dosimetric point of view. With the advent of colour centre lasers based on different types of F-aggregate centres in alkali halides, it has become important to explore all possible means of creating sufficiently large population of the lasing colour centre at an amenable temperature. Extensive reviews on colour centre lasers are available [5, 6] and these deal mainly with the studies on lasers based on $F_A/F_2^+/F_2^-$ colour centres.

A lasing system based on F_3^+ centre, though feasible, has not been studied in detail. Recent reports refer to the feasibility of F_3^+ laser action in LiF single crystal, wherein, low temperature electron bombardment [7, 8] or optical conversion at 77 K [9] has been used for achieving population build-up of F_3^+ centres. Russian workers [10] have also reported Einstein's spectral coefficients for the F_3^+ centre with reference to laser action. In the present work, significantly large build-up of F_3^+ centres has been achieved in optical LiF single crystals at room temperature itself, using a XeCl excimer laser. The work carried out here also includes detailed studies on the thermal stabilities of F-aggregate centres and the mechanism of optical conversion processes.

2. Experimental

Optical quality single crystals of LiF were grown in vacuum (10^{-5} torr) by Stober's method [11] using indigenously developed facilities [12]. During the crystal growth, a cooling rate of 4°C/h was maintained up to 50°C below the melting point and thereafter the rate was stepped up to 20°C/h in stages.

Colour centres were produced in the LiF crystals by irradiation at room temperature using a ^{60}Co gamma source (0·4 M rad/h). These were identified by their well reported spectral characteristics [13–16]. Optical absorption spectra were recorded on a Beckman Du-7 spectrophotometer, while excitation and luminescence spectra were recorded on a Hitachi F-3010 spectrofluorimeter. The optical conversion of colour centres both at 300 K and 77 K was studied using a 308 nm XeCl excimer laser (10 mJ pulse energy, 50 Hz). Thermal stabilities of colour centres were investigated by successively heating the same crystal for 15 min at different temperatures up to 300°C in steps of 25°C. The changes brought about in the population of different colour centres separately by laser irradiation and due to heat treatment were identified from the spectral studies. Using the data obtained on thermal stabilities of different colour centres, specific centres were annihilated by heat treatment and the effects of subsequent laser irradiation were studied in detail.

3. Results and discussion

3.1 *Laser induced conversion of colour centres*

Optical absorption spectra were recorded for the same gamma irradiated crystal at room temperature (a) prior to laser exposure, (b) immediately after laser exposure and (c) 24 h after laser exposure (figure 1). Identical spectra were obtained for the crystals on exposure to laser irradiation at 77 K. As seen from the figure, prior to laser exposure the crystal showed absorption bands with peak positions at 250, 310, 380

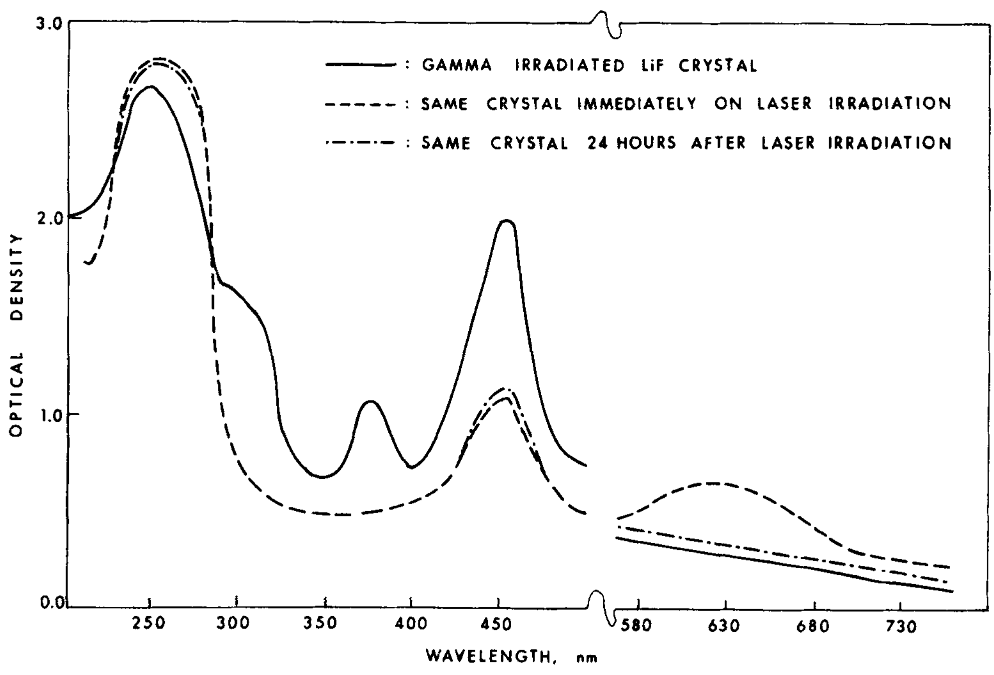

Figure 1. Optical absorption spectra for gamma irradiated LiF crystal at room temperature (a) prior to laser exposure (b) immediately after laser exposure and (c) 24 hours after laser exposure.

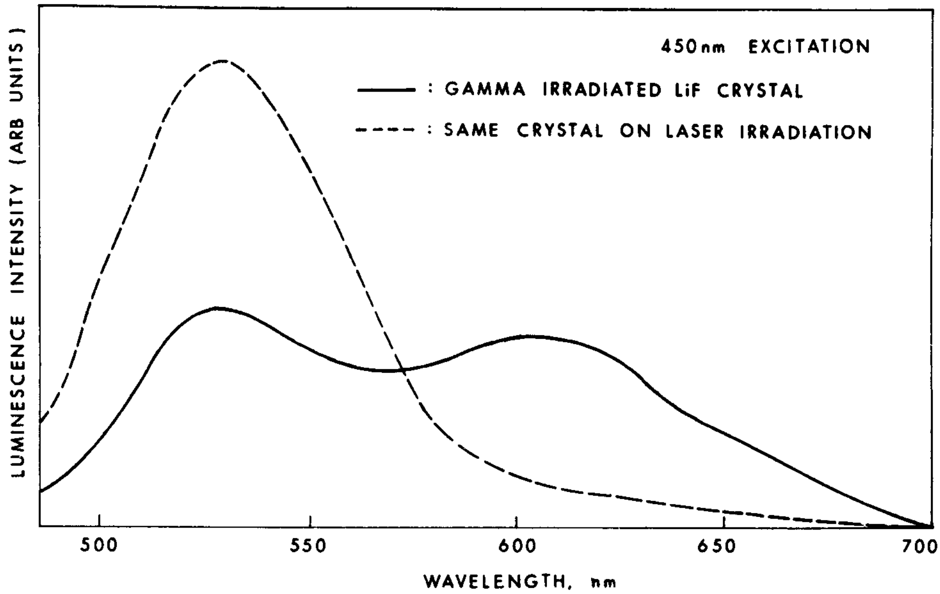

Figure 2. Luminescence spectra with 450 nm excitation for gamma irradiated LiF crystal (a) prior to laser exposure and (b) immediately after laser exposure.

and 450 nm. Of these, a peak at 250 nm corresponding to F centre showed significant increase in intensity on laser exposure at both the temperatures. The peaks at 310 and 380 nm corresponding to F_3 centres, on laser exposure, showed drastic reduction in intensity at both the temperatures. The peak around 450 nm was a composite one corresponding to F_2 and F_3^+ colour centres and also showed significant reduction on laser exposure at two temperatures. An additional peak at 630 nm, which is known to correspond to F_2^+ centre was observed only on laser exposure implying its formation due to optical conversion. On storage the peak at 630 nm was not observable while the peak around 450 nm showed some rise in intensity over the one observed immediately on laser exposure.

The luminescence spectra recorded with 450 nm excitation for the gamma irradiated crystal before and after laser exposure at 300 K is shown in figure 2. As seen from this figure, luminescence intensity around 620 nm corresponding to F_2 centres showed significant reduction, while, luminescence intensity at 530 nm corresponding to F_3^+ centres showed a four-fold increase on laser exposure. On storage of the laser irradiated crystal for 24 h, there was no significant change in the luminescence spectrum in comparison to the one recorded immediately after laser irradiation.

These observations have revealed that on 308 nm laser exposure at 300 K (i) F, F_2^+ and F_3^+ colour centre populations increase and (ii) F_2 and F_3 colour centre populations decrease. On storage of laser irradiated crystal, F_2^+ population decreases significantly leading to further rise in F_3^+ population.

In contrast to 337 nm N_2 laser irradiation reported for the optical conversion [9], the present work is based on the use of 308 nm radiation from XeCl laser. The excitation spectrum recorded at room temperature for the gamma irradiated crystal by monitoring F_3 emission has shown that 308 nm excitation would correspond to resonant absorption for F_3 centres, while, 337 nm would not be so. This would, in turn, reflect in the higher efficiency of the conversion process of F_3 centres with 308 nm laser irradiation.

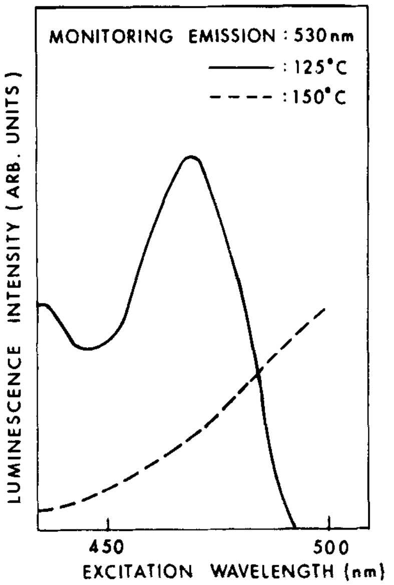

Figure 3. Excitation spectra for F_3^+ centers in gamma irradiated LiF crystal before and after annihilation.

3.2 *Thermal stability of F-aggregate centres in LiF crystal*

Studies carried out on thermal stability of different colour centres have revealed that F_2, F_3 and F_3^+ centres are stable up to 200°C, 250°C and 125°C respectively. A typical excitation spectrum for F_3^+ centres revealing this aspect is shown in figure 3. The feasibility of room temperature operation of F_3^+ centre based laser is evident from the thermal stability of these centres up to 125°C.

3.3 *Mechanism for laser induced conversion of F-aggregate centres*

As seen from the above discussion, laser induced conversion of F-aggregate centres is an involved process with number of changes occurring simultaneously. Additional investigations were carried out to ascertain the pathways for the conversion process. Lithium fluoride crystals of identical dimensions were gamma irradiated at room temperature and by annealing these crystals one at each of the following temperatures viz. 100, 150, 225 and 275°C, for 15 min, different colour centres viz. F_2^+, $F_3^+ + F_2^+$, $F_2 + F_3^+ + F_2^+$ and $F_3 + F_2 + F_3^+ + F_2^+$ were thermally destroyed respectively. Using these crystals laser induced changes were followed by recording absorption and luminescence spectra before and after laser irradiation. The results of these investigations are tabulated below.

Annealing temperature, °C	Colour centers destroyed	Colour centers present	Laser induced change
100	F_2^+	F, F_2, F_3, F_3^+	Increase in F, F_3^+ Decrease in F_2, F_3 Generation of F_2^+
150	F_3^+, F_2^+	F, F_2, F_3	Increase in F Decrease in F_2, F_3 Generation of F_2^+, F_3^+
225	F_2, F_2^+, F_3^+	F, F_3	Increase in F Decrease in F_3 Generation of F_3^+
275	F_2, F_3, F_3^+, F_2^+	F	No change

These observations reveal that (i) F_2^+ centres are formed only when F_2 centres are present in the gamma irradiated crystal prior to laser irradiation and (ii) similarly F_3^+ centres are formed by laser irradiation in gamma irradiated crystal only if F_3 centres are present. Thus the optical conversion process is one of the photoionization, wherein,

$$F_3 \xrightarrow{\text{308 nm laser irradiation}} F_3^+ + e^-$$

and

$$F_2 \xrightarrow{\text{308 nm laser irradiation}} F_2^+ + e^-$$

Free electrons released in these processes are captured at anionic vacancy sites in the crystal leading to formation of additional F centres.

Such a photoionization process for the formation of F_2^+ centres is well reported for alkali halide crystals using two-step photoionization process [5]; however, the process is usually carried out at 77 K due to instability of F_2^+ at room temperature. Similarly the photoionization process for F_3 centres has also been reported to occur only at 77 K using 337 nm N_2 laser excitation [9], while the present studies show that using 308 nm XeCl laser two-step photoionization process can be carried out at room temperature thereby increasing the feasibility of F_3^+ based lasers.

4. Conclusion

Present work conclusively shows that (i) Population build-up of F_3^+ in gamma irradiated lithium fluoride crystal can be achieved at room temperature using 308 nm XeCl excimer laser by photoionization process, (ii) F_2 centre population, detrimental to F_3^+ laser action, due to its overlapping absorption band, can be reduced simultaneously by 308 nm laser photoionization and (iii) F_3^+ laser action is feasible at room temperature as these centres are thermally stable up to 125°C.

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