

THE EFFECT OF THE ANNEALING TEMPERATURE IN THE LUMINESCENCE CHARACTERISTICS OF THE PURE CsI SCINTILLATOR CRYSTAL.

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ABSTRACT

The experimental results on the emission spectra for a pure CsI crystal under gamma excitation and alpha-particle excitation seem to provide a strong argument in a favour of the intrinsic vacancy model on the origin of the slow emission spectra. The decrease of the slow component after the crystal growth is explained in terms of the reduction in the number of vacancies, which are mainly resulted from temperature equilibrium conditions at crystal growth. By observing the quenching of the heat treatment was found that the optimum annealing temperature should be around 100°C, in order to suppress the slow component. The heat treatment of annealing process for CsI crystal at 75°C has resulted in a significant decrease in the slow emission component compared to the crystal kept at room temperature. The decay times for fast component were of about 10 ns and 36 ns, while the decay time for slow component varied of 1 - 4 μ s from sample to sample.

INTRODUCTION

It has been reported in our previous papers [1,2] that pure cesium iodide (CsI) exhibits a fast scintillation emission at ~305 nm, where the time structure can be characterized mainly by two decay times of 10 ns and 35 ns. The fast scintillation property with its high density (4,5 g/cm³) makes CsI one of the most attractive materials in high resolution electromagnetic calorimeter at high counting rates as well as for positron tomography [3,4]. Pure CsI, therefore offers a promising detection medium for large scale high rate detectors in high energy physics and medical application.

One of the disadvantages of pure CsI scintillator for application in these fields is the existence of a slow emission component with a decay time of ~ 1 μ s which forms a continuous emission spectrum in a wavelength region of 380-600nm. The peak position and its intensity depend on sample crystal and on the methods of crystal growth [5,6]. The slow component causes deterioration of the time resolution, when used as scintillator, for the high counting rate [7]. Therefore the suppression of the slow decay time is of practical interest. A considerable effort has been under way for a number of years by several manufacturers to produce such crystal without the slow

component. There has been, as far as the authors know, no report on the method to eliminate this slow component.

In the present work the authors describe the results of the study of heat treatment of CsI crystal at different temperatures, after crystal growth. The aim is to find a way of eliminating the slow component by annealing process. The CsI samples were submitted to different temperatures to observe the effect of the annealing in the emission luminescence spectra. After determining the optimum annealing temperature, the CsI samples were stored in this temperature and systematic measurements on the emission spectra were made over a period of about three months.

PHYSICAL ORIGIN OF THE SLOW COMPONENT

In the early stage of development of pure CsI scintillators it is believed that the slow component is partly related to impurities in the crystal[5,8]. Recently, Utts and Spagno reported[5] that the origin of the slow component at peak positions of 420 nm and 500 nm is related to defects or unknown impurity other than K, Na, Tl, Rb or F which they have analysed in their crystals. It was reported many years ago[9] that iodine vacancies act as emission center of 420nm band from the CsI crystal, which is overheated at vacuum.

Bates observed the emission in the wavelength region of 350-550 nm from the sample in which strain was induced by cooling [10]. This luminescence was attributed to the emission from excitons annihilating at the site of such defects like I-vacancy or F-center. It was reported that iodine vacancies act as emission centers generating a 410 nm emission band in the CsI crystal, which was overheated in vacuum and then crystallized [9,11]. Gwin and Murray reported that the luminescence forming a broad band centered near 470 nm is associated with crystalline imperfections [12].

Depending upon their effective charge polarity, vacancies in CsI crystal can act as either electron or hole traps in crystal. There are two types of vacancy formation processes: the intrinsic and extrinsic processes. In the intrinsic processes the number of the vacancy is determined by crystal temperature. In the extrinsic process, on the other hand, the number of vacancy is determined by the concentration of those impurities which have different charge from the host. These electrons (hole) trapped at the site of the vacancies could recombine with free holes (electrons) generated, for example, by ionizing charged particles and may result in the emission of the slow component.

Here, we consider the possibility of the iodine vacancies be the origin of the slow component. Iodine vacancies can diffuse in crystal by changing their positions with the nearest neighbour atoms and finally disappear in the crystal surface. Since the number of iodine vacancies is smaller in the surface than that in the bulk of the crystal, it is expected that the contribution of the slow component from near crystal surface is less than that in the bulk. In order to ascertain this statement we used ^{241}Am alpha

source for the excitation of the crystal layer and gamma rays from ^{137}Cs source for the bulk of the crystal. The range of the 5.5 MeV alpha particle is about 25 μm .

The crystal used here were grown by the vertical Bridgman method using a quartz crucible in a halogen atmosphere. Starting powder material, obtained from Metal Gesellschaft, 99,995 pure, was purified under vacuum at about 200°C. The samples were cut sizing about 8 mm x 10 mm (length x diameter) and polished. The emission spectra were measured with a monochromator (JASCL, FP550A) with a wavelength resolution of 20 nm.

Figure 1(a) shows a typical emission spectrum from the bulk of the pure CsI crystal under electron excitation and Fig. 1(b) the surface layer of the same CsI crystal under alpha particle excitation. It is seen from these figures that the dominant 450 nm band observed from the bulk of the crystal is not observed from the surface layer of the crystal, as expected.

A new surface layer is obtained by etching this CsI crystal by washing it with water, removing of about 100 μm of the crystal near surface layer, which was immediately irradiated with the alpha particle. As shown in Fig. 1(c) the 450 nm band is enhanced in this new surface layer. The increase in the 450 nm band in the washed crystal may be attributed to the difference of densities of the iodine vacancies between the old surface layer and the new surface layer.

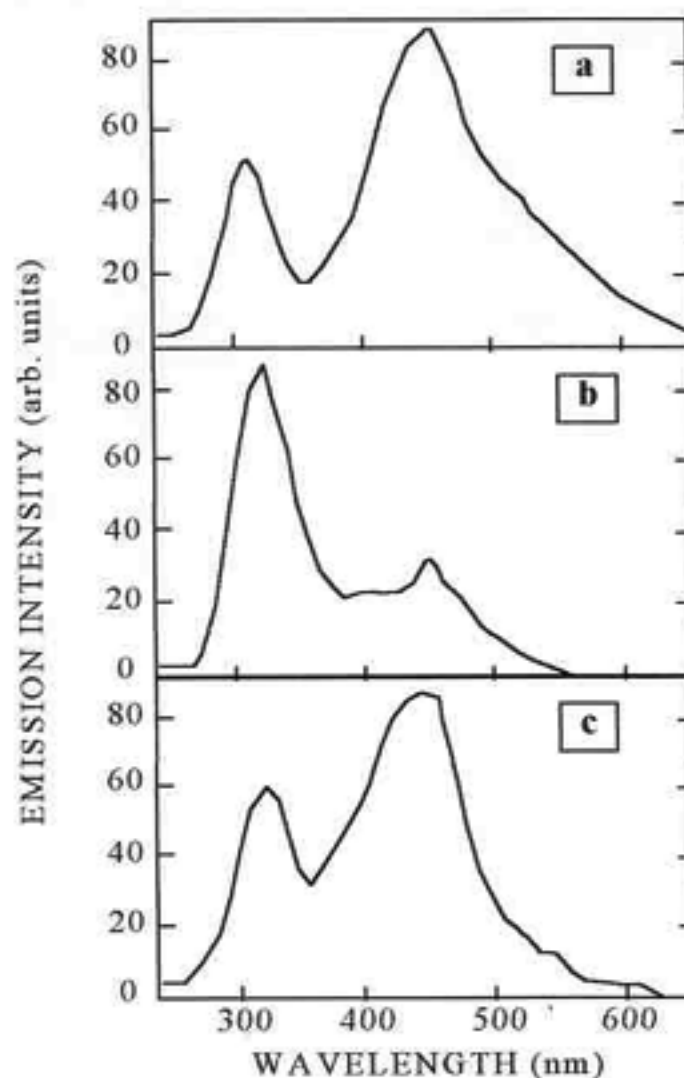


Fig.1. Emission spectra from the CsI crystal under electron excitation (a) and under alpha-particle excitation (b) and from the same CsI crystal with new layer surface under alpha-particle excitation (c).

The above observation supports the statement that the 450 nm band is related to iodine vacancies, since as described before, intrinsic vacancies could diffuse through the lattice and are annihilated at the surface, while extrinsic vacancies can not diffuse to the surface. An uniform distribution of the extrinsic vacancy should be expected in the crystal volume, then the number of the extrinsic vacancies should not change after the crystal growth. In this case, the intensity of the slow component must be constant.

OPTIMUM ANNEALING TEMPERATURE

It is almost certain that the intrinsic vacancies existing at high temperature of the crystal growth are frozen at room temperature (RT) due to an insufficient time for annealing after the crystal growth. In this case, the number of the intrinsic vacancies should decrease with the time gradually, approaching to the value determined at RT. So, it is expected a decrease in the intensity of the slow component in the crystal, which origin is due to the intrinsic vacancies.

Since the diffusion process of the intrinsic vacancies enhanced at the higher temperature it should result in a faster decrease of the number of the intrinsic vacancies, then the annealing process could be considered as a promising way to reducing the slow emission component. However, the number of the intrinsic vacancies is known to increase with increasing temperature as well. Therefore, the optimum annealing temperature, i.e. the temperature more favourable for the diffusion of iodine vacancies must be found. The thermal quenching should not occur in practice when the annealed crystal is cooled to room temperature.

To determine the optimum annealing temperature, one crystal, grown three years prior to this measurement, was used for the study of thermal quenching. This crystal presented the slow component emission with an intensity extremely low. This crystal was heated to different temperatures T ($T = 75, 100, 150, 200, 250$ and 300°C) for one hour. Following each heat treatment, the crystal was quenched to room temperature and the emission spectrum from the crystal bulk was measured, after each quenching process, with a monochromator (JASCL, FP550A) with a wavelength resolution of 20nm, by gamma ray excitation from ^{137}Cs at room temperature.

Figure 2 shows emission spectra after thermal quenching at different temperatures. The almost complete suppression of the slow component was observed at a thermal quenching of 75°C and 100°C . With the thermal quenching higher than 150°C , the increase in the intensity of the 450 nm were observed. On the other hand, no significant difference was observed in the fast component at the peak of 310 nm. From these results we could conclude that the optimum temperature for the heat treatment should not be higher than 150°C . Above this, the thermal breaching occurs, increasing the slow component in the crystal, while no change in the intensity

for the fast component band was observed for all temperature studied.

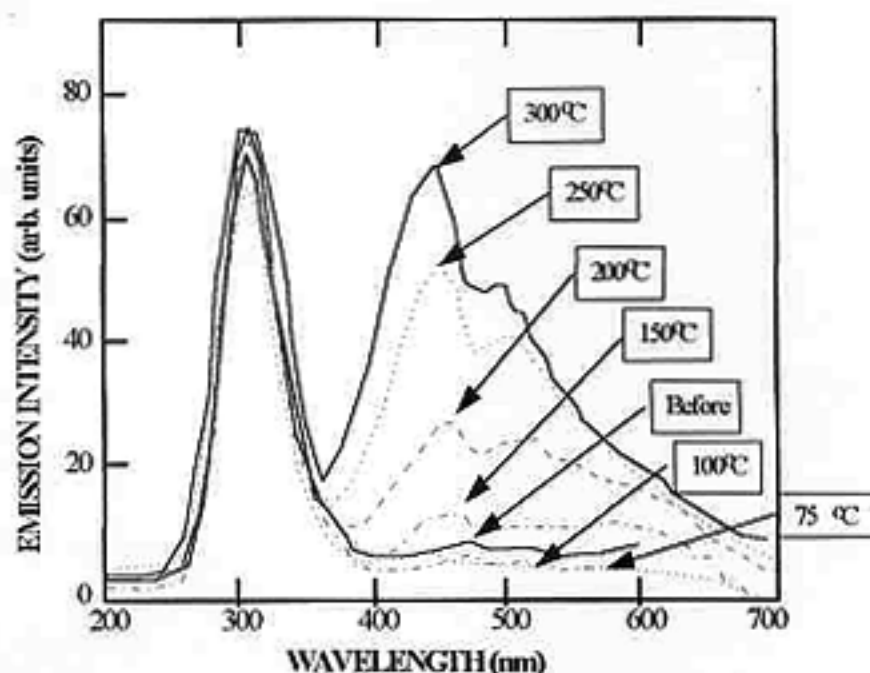


Fig.2. Emission spectra from CsI crystal, which was heated to temperatures of $75, 100, 150, 200, 250, 300^\circ\text{C}$.

HEAT TREATMENT

In order to decrease the contribution of the slow component it is necessary to remove iodine vacancies in the crystal. As describe before, the intrinsic vacancies could be eliminated by annealing the crystal. In this experiment four sample crystals were used. They are denoted A1, A2, B1 and B2. The samples A1 and A2 were originally part of the same crystal and as well as B1 and B2. The crystals A and B were cut by half and the first part and the last part were called A1 (or B1) and A2 (or B2), respectively. The crystals growths of the samples were completed three days prior to the experiments. The emission spectra of these crystals were continually measured over a period of three months. During this period the samples A1 and B2 were stored at 75°C in a furnace, while the samples A2 and B1 were stored at room temperature (RT). All the samples were kept in environmental atmosphere. The measurements of emission spectra from the crystal bulk of those samples under gamma-ray excitation from ^{137}Cs were made at room temperature.

Figure 3 shows the observed emission spectrum of the sample crystal A1 before a heat treatment and after the heat treatment of 75°C for storage periods of 1, 4 and 16 days. Figure 4 shows the emission spectra of sample A2 stored at room temperature after 3, 16, 25 and 91 days of the crystal growth completion.

It is clearly seen from these figures that the intensity of the slow emission component decreases with increasing in the storage period both for 75°C and RT. It should be noticed here that the sample stored at 75°C had a higher rate of decreasing the slow component intensity than that stored at RT. Similar emission spectra were

observed for the samples of B1 and B2, stored at RT and 75°C, for a period of three months.

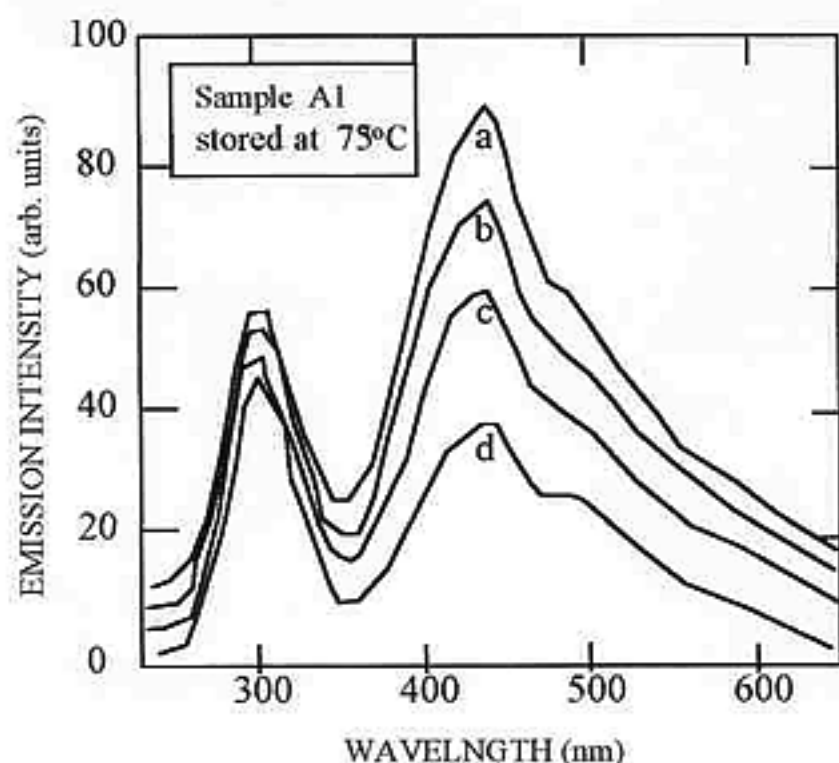


Figure 3. Emission spectra from the sample A1 before the heat treatment (a) and after the heat treatment at 75°C with the storage periods of one day (b), four days (c) and 16 days (d). To separate the spectra corresponding to different days of measurement, the spectra a, b and c were shifted vertically by an amount 3RS, 2RS and RS, respectively.

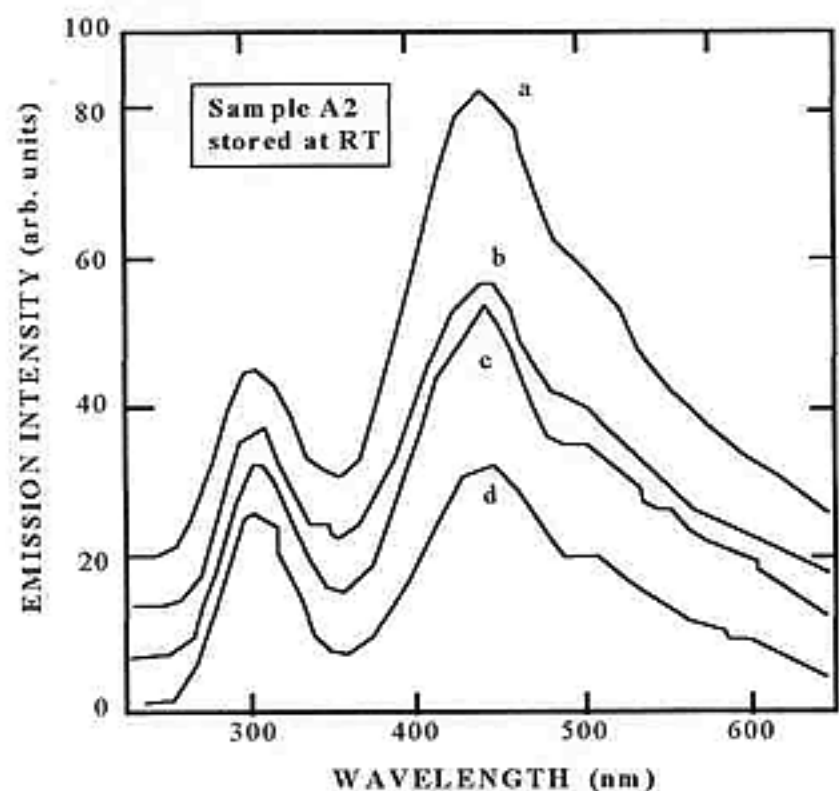


Figure 4. Emission spectra from the sample A2 stored at RT which were measured three days (a), 16 days (b), 25 days (c) and 91 days (d) after the last day of the crystal growth. To separate the spectra corresponding to different days of measurement, the spectra a, b and c were shifted vertically by an amount 3RS, 2RS and RS, respectively.

Fig. 5 shows the variations of the intensity ratios S/F of the crystals against the period. Here, S and F denote the peak intensities of the slow emission component and the fast component, respectively.

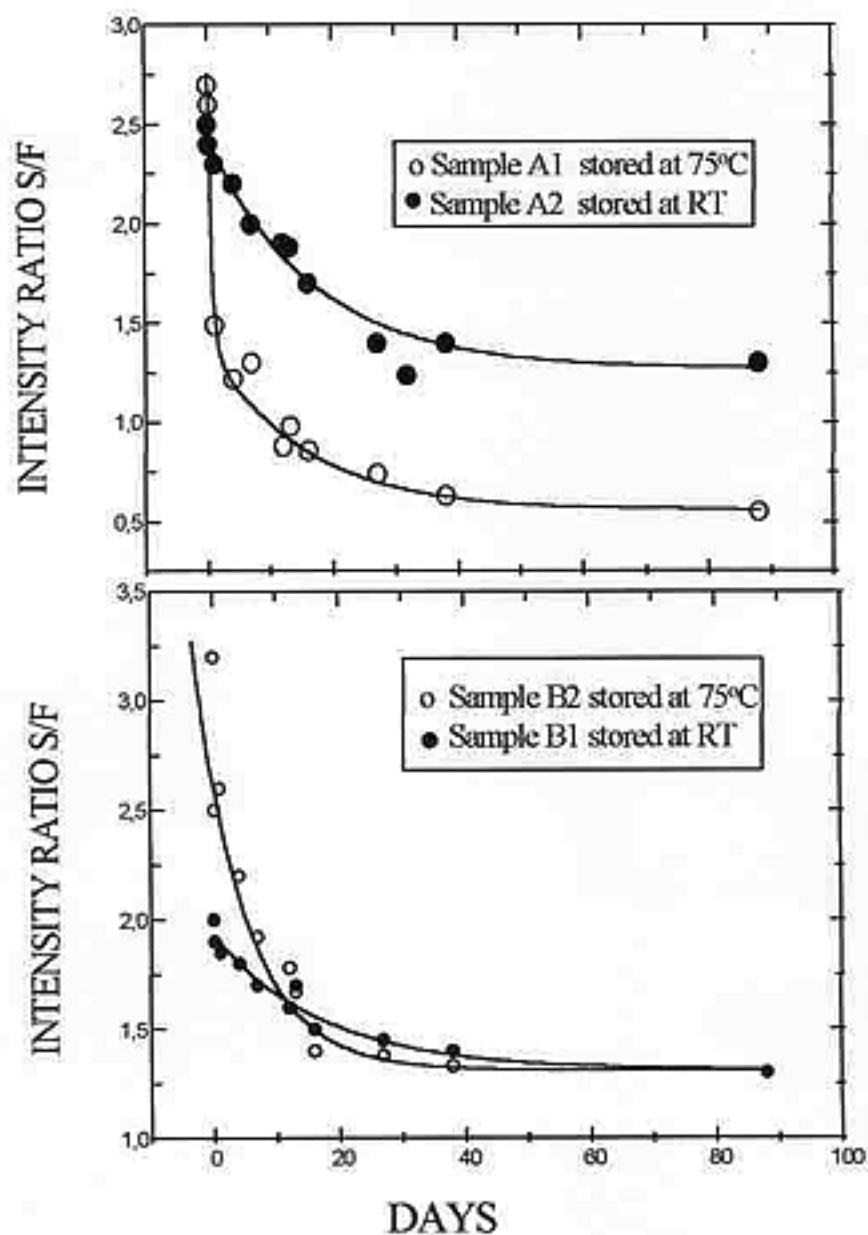


Figure 5. The variations of the peak intensity ratio S/F for the samples A1 and B2 stored at 75°C and A2 and B1 stored at room temperature during 3 months.

As it can be observed in fig. 5, for samples kept at 75°C prompt decreases occur in the intensity ratios S/F within the heat treatment of one day. After the prompt decreases the ratios S/F tended to decrease more slowly and then saturate to constant values in the present observation period of 16 days. On the other hand, the S/F ratios exhibited only slow decreases, which eventually saturate to constant values after 90 days.

These phenomena found in the present study could probably be caused by the reduction in the number of the intrinsic vacancies existing in the samples. These vacancies decrease as time passes due to the diffusion process through the lattice which eventually lead them to annihilate the surface. In accordance with the intrinsic vacancy diffusion model, the decrease in the luminescence intensity of the slow component should be more enhanced at a higher temperature, since the diffusion process is more effectively proceeded. These results support the model that the origin of the slow component is closely related to the intrinsic vacancies.

DECAY TIME MEASUREMENTS

The decay time were measured by the single photon counting technique. The experimental apparatus is similar describe in ref. [7]. Figure 6 shows the typical decay curves measured for the fast component band at 310nm.

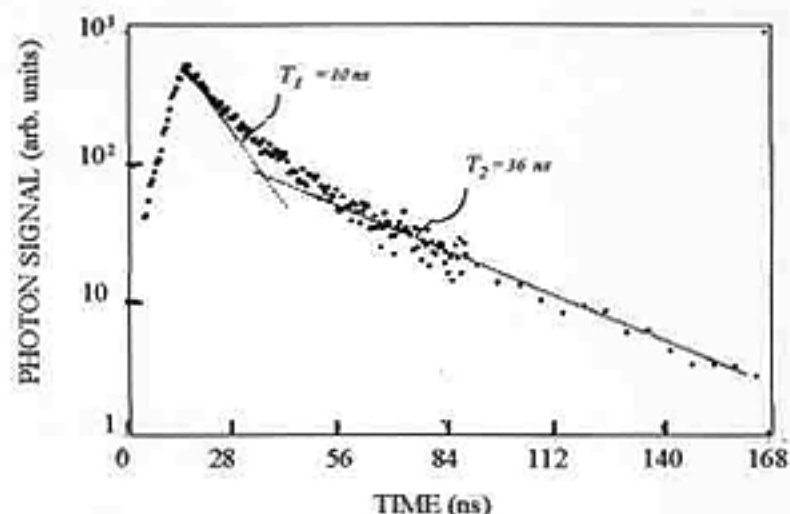


Fig. 6. Typical decay curve of the 310 nm emission

The observed decay curves are fitted a two exponential function with decay time constants of τ_1 and τ_2 , i.e. $(I_1/\tau_1) \exp(-t/\tau_1) + (I_2/\tau_2) \exp(-t/\tau_2)$. The fitted values were found to be for $\tau_1 = 10$ ns and $\tau_2 = 36$ ns and the relative intensity ratio I_1/I_2 was 3. The 450 nm band had a decay time of 1 - 4 μ s, which varied from sample to sample. These values of the decay times are in good agreement with that reported in the literature [1,2,6].

In short, it should be emphasised from these results that the annealing temperature should be not be higher than 150°C. The diffusion of the iodine vacancies of the crystal bulk to surface was proved to more favourable, decreasing the slow component, when treated until this temperature. Above this temperature the thermal quenching occurs, increasing the slow component in the crystal, while no change in the intensity for the fast component band was observed for all temperatures studied.

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