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Suppression of the slow emission component in pure CsI by heat treatment

M.M. Hamada ^{a,1}, Y. Nunoya ^{a,2}, S. Kubota ^{a,*}, S. Sakuragi ^b^a Rikkyo University, Nishi-Ikebukuro 3, Tokyo 171, Japan^b Union Materials Inc., Tonemachi, Kitasoma, Ibaraki 300-16, Japan

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Abstract

The heat treatment of annealing process for pure CsI crystals at 75°C has resulted in a significant decrease in the slow emission component compared with the crystals kept at room temperature. By observing the quenching of the heat treatment, it is found that the annealing temperature to suppress the slow emission component should not be higher than 150°C. The experimental results on the emission spectra of pure CsI crystal under gamma-ray excitation and alpha-particle excitation seem to provide a strong argument in favor of the intrinsic vacancy model on the origin of the slow emission component.

1. Introduction

It has been reported in our previous papers [1,2] that pure cesium iodide (CsI) exhibits a fast scintillation emission at ~ 305 nm, of which 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 calorimetry at high counting rates as well as for positron tomography [3,4]. Pure CsI can be produced by employing the technology similar to that used for CsI(Tl). The latter was developed and produced in multi-ton quantities by Horiba Ltd. in the CLEO-II project of Cornell University [5]. Pure CsI, therefore, offers a promising detection medium for large scale high-rate detectors in high energy physics, nuclear physics and medical applications.

One of the main concerns of a pure CsI scintillator when applied to these fields is, however, 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 380–600 nm. It has been reported that the peak position of this emission band depends on sample crystals [6] and its intensity depends on the methods of crystal growth [7]. A considerable effort has been under

way for a number of years by several manufacturers to produce such crystals without the slow emission component. There has been, as far as the authors know, no report on the method to eliminate this slow component.

There have been several papers on the origin of the slow emission component. In the early stage of developing pure CsI scintillators, it was believed that the slow component was partly related to some impurities in the crystal [6,8]. Utts and Spagno reported that the origin of the slow emission component at peak positions of 420 nm and 500 nm was related to an unknown impurity other than K, Na, Tl, Rb or F and/or to defects [6].

Bates observed the emission in the wavelength region of 350–550 nm from the sample in which strain was induced by cooling [9]. This luminescence was attributed to the emission from excitons annihilating at the site of such crystal 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 [10,11]. In 1963, 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 the extrinsic processes. In the intrinsic process 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 (holes) trapped at the

* Corresponding author.

¹ On leave from IPEN/CNEN-SP Travessa R n^o. 400-Cidade Universitária, São Paulo, Brazil.

² Present address: Naka Fusion Research Establishment, Japan Atomic Energy Research Institute, Naka, Ibaraki 300-02, Japan.

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.

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. If, therefore, the intrinsic vacancy centers are responsible for the origin of the slow luminescence, a decrease in the intensity of the slow component should be observed. On the other hand, the number of the extrinsic vacancies should not change after the crystal growth. If, therefore, the extrinsic vacancies are responsible for the origin of the slow component, the intensity is expected to be highly constant.

In order to determine which is responsible for the luminescence mechanism of the slow component associated with either intrinsic vacancy centers or extrinsic vacancy centers, systematic measurements on the emission spectra of CsI samples were made over a period of about three months after the crystal growth. In these measurements, the samples under investigation were stored at two different temperatures to observe the effect of the annealing. In addition, the measurements of emission spectra were carried out at different positions of a crystal to study the difference in the concentrations of the vacancies in the crystals.

2. Experimental

The crystals used in this work were grown in accordance with the vertical Bridgman method using a quartz crucible in halogen atmosphere. The starting powder used with a purity of 99.99% was obtained from Metal Gesellschaft K.K., Germany. Before starting the crystal growth, the powder was further purified by evacuating and heating it in the quartz crucible at about 150°C for two hours to remove mainly residual water. After the purification process, the quartz crucible was sealed off by gas touch filling with argon gas. Crystal samples around 10 cm long were obtained with a growth rate of 2 mm/h.

To study the time variation of the intensity for the slow component, five samples of the pure CsI crystal were used. They are denoted AF, AL, BF, BL and C, respectively. The samples AF and AL were from the first part and the last part of the crystal called A, and samples BF and BL from the first and the last part of the crystal B, respectively. The crystal growths of the samples A and B were completed three days prior to the experiments, while that of the sample C as long as three years. The five samples were cut and polished in cylindrical shape of about 8 mm in diameter and about 10 mm in height.

The emission spectra of these crystals were continually measured over a period of three months. During this period the samples AL and BF were stored at RT, while the samples AF, BL and C were at 75°C in a furnace. All the samples were kept in environmental atmosphere. The three samples AF, BL and C were taken from the furnace and were cooled to RT to measure the emission spectra. After carrying out the spectrum, the samples were placed back in the furnace for further heat treatment.

After measuring the three samples of AF, BL and C at 75°C for 21 days, they were temperature cycled between a high temperature T at one hour and cooled to RT in order to study the effect of the thermal quenching on the emission spectra. T was set to be 100, 150, 200, 250 and 300°C. After this heat treatment, the crystals were again kept at 75°C.

The emission spectra were measured with a monochromator (JASCL, FP550A) having a wavelength resolution of 20 nm. The observed spectra were corrected for second-order light from the grating. The gamma-rays from a RaD-Be source were used to excite the crystals. Furthermore, 5.5 MeV alpha-particles from a ^{241}Am source were also used to excite the crystal near surface. The range of 5.5 MeV alpha particles in CsI crystal is about 20 μm , while the absorption length for the above gamma rays is about 5 cm.

3. Results and discussions

3.1. The time variation of the intensity for the slow component

Fig. 1 shows the observed emission spectrum of the sample crystal AF before a heat treatment and after the heat treatment of 75°C for storage periods of 1, 4 and 16 days. The heat treatments were started three days after the crystal growth completion. The emission spectra observed of the sample AL stored at RT are shown in Fig. 2 for storage periods of 3, 16, 25 and 91 days after the crystal growth. In order not to overlap each other, the observed emission spectra have been shifted vertically by an amount of 3RS, 2RS and RS, respectively. The magnitude of RS for each curve is indicated in the figure caption.

It is clearly seen from Fig. 1 that the luminescence bands are observed near 305 nm (fast emission component) and near 440 nm (slow emission component). 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 has a higher rate of decreasing the slow component intensity than that stored at RT. Similar emission spectra were observed for the samples of AL and BF, stored at 75°C and RT, for a period of three months.

Fig. 3 shows the emission spectrum of the crystal C, which was grown three years prior to this measurement.

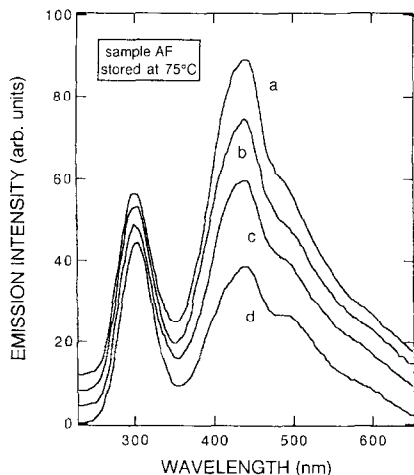


Fig. 1. Emission spectra from the sample AF before the heat treatment (a) and after the heat treatment at 75°C with the storage periods of one day (b), four days (c) and 16 days (d). The spectrum (a) was measured after three days from the last day of the crystal growth. To separate the spectra corresponding to different days of measurement, the spectra a, b, and c were shifted vertically by an amount 3RS, 2RS and RS, respectively. Here, RS is set to equal to 3.7 in this figure.

We surprisingly found that the slow component emission has an extremely low intensity in the emission spectrum. This suggests that the storing of pure CsI crystals even at RT for several years after the growing processes can be an effective way of diminishing the contribution from the slow luminescence component.

These remarkable phenomena found in the present study could probably be caused by the reduction in the number of the intrinsic vacancies existing in the samples with time due to the diffusion process through the lattice which eventually lead them to annihilate at the surface. In accordance with the intrinsic vacancy diffusion model, the

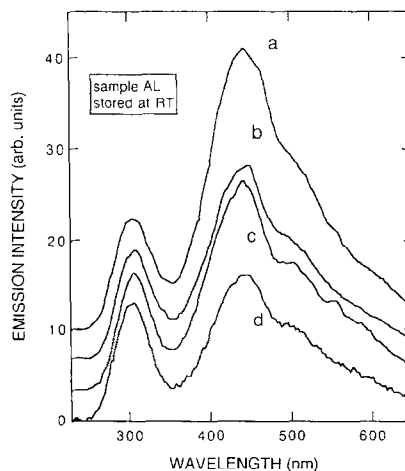


Fig. 2. Emission spectra from the sample AL stored at RT, which were measured three days (a), 16 days (b), 25 days (c) and 91 days (d) after the last day of the crystal growth. To separate the spectra corresponding to different days of measurement, the spectra a, b, and c were shifted vertically by an amount 3RS, 2RS and RS, respectively. Here, RS is set to equal to 3.3.

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. Fig. 3 clearly displays this expected tendency, supporting the model that the origin of the slow luminescence component is closely related to the intrinsic vacancies.

Table 1 summarizes the peak intensity ratios, S/F , of the sample crystals before and after the heat treatment. Here, S and F denote the peak intensities of the slow emission component and the fast component, respectively. Fig. 4 shows the variations of the intensity ratios S/F of the crystals against the period. The major features drawn from the figures are:

- 1) *Samples AF and BL kept at 75°C.* There exist

Table 1
The variation of the peak intensity ratios S/F

Samples	Crystals	Temperature	S/F ^e		Reduction		Fitted parameters	
			before	after 16 days	after 16 days [%]	after 90 days [%]	decay time [days]	constants
AF	A	75°C	1.7 ^a	0.86	49	20 ^c	0.8, 23 ^c	0.32 ^c
AL	A	RT	2.5 ^a	1.6	36	50	14 ^d	1.3 ^d
BL	B	75°C	3.4 ^a	1.4	59	20 ^c	0.2, 20 ^c	0.6 ^c
BF	B	RT	1.9 ^a	1.6	16	70	9 ^d	1.4 ^d
C	C	75°C	0.23 ^b	0.13	43	43 ^c	0.1 ^c	0.1 ^c

^a Measured after three days from the last day of the crystal growth.

^b Measured after about three years from the last day of the crystal growth.

^c The variations of S/F ratio upto 16 days were fitted to a sum of two exponential decay curves and a constant, through which the ratio after 90 days were extrapolated.

^d The variations of S/F ratio upto 90 days were fitted to a sum of a single exponential decay curve and a constant.

^e The experimental uncertainty is 10%.

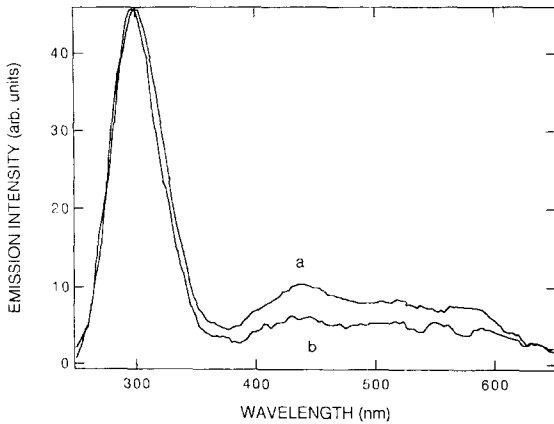


Fig. 3. Emission spectra of the sample C before (a) and after (b) the heat treatment at 75°C for storage period of one hour. The spectrum (a) was measured after about three years from the end of the crystal growth.

prompt decreases in the intensity ratios S/F within the heat treatment of one day. After the prompt decreases the ratios S/F tend to decrease more slowly and then saturate to constant values in the present observation period of 16 days.

2) *Samples AL and BF kept at room temperature.* The S/F ratios exhibit only slow decreases, which eventually saturate to constant values after 90 days.

3) *Sample C kept at 75°C.* A rapid decrease of a factor of 2 in the S/F ratio was observed with the heat treatment of one hour. After this, no appreciable change in the S/F ratio was observed over the observation period of 16 days.

The observed time variations of the S/F ratio for the crystal samples AF and BL of the samples with heat treatment within 16 days were fitted to curves which consisted of two exponential functions and one constant. The fitted curves are shown in Fig. 4 and the fitted parameters are summarized in Table 1. The two time constants, τ_f and τ_s , obtained from the fitting procedure were 0.2–0.8 day and 20–23 day, respectively, each controlling the time variation of S/F ratio in different time scales. The extrapolated S/F values of the samples AF and BL at 90 days were found to be 0.32 and 0.6, respectively. These S/F values were about 20% of that before the heat treatment.

A combined function of a single exponential curve and a constant was used to fit the variations of the S/F ratio for the samples AL and BF over the observation period of 90 days. The fitted results are shown in Fig. 4 and in Table 1. The S/F values at 90 days were reduced to about 50–70% of the initial values. These reductions were apparently larger than those (20%) in the samples with heat treatment. This result demonstrates that the heat treatment is effective to suppress the slow emission component in a given time.

3.2. Surface phenomenon

Excitation of crystal bulk due to gamma-rays gives rise a strong slow luminescence component as shown in Fig. 5a. This spectrum was obtained for the CsI crystal stored for about three months after the crystal growth.

On the contrary the intensity of the slow component observed when the same crystal is irradiated with 5.5 MeV alpha-particles was considerably smaller than that under the bulk excitation, as shown in Fig. 5b.

Because of the very short range of the alpha particles in the crystal as mentioned before, it was speculated that the

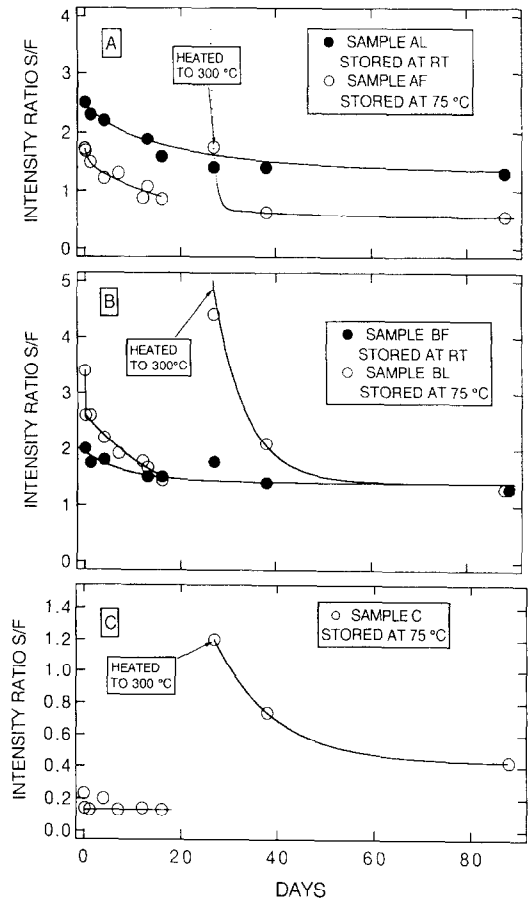


Fig. 4. The variations of the peak intensity ratio S/F for the samples AF, BL and C stored at 75°C over the observation period of 16 days. On the 21st day, those samples were temperature cycled between the high temperatures of 100, 150, 200, 250 and 300°C for one hour and quenched to room temperature. After this, those samples were stored at 75°C. The samples AL and BF were stored at room temperature over a period of three months. The emission spectra was measured after three days from the crystal growth. Solid curves superimposed on the data of the samples AL, BL, AF and BF are the fitted curves (see text). The curves for AF and BF from 21 days to 90 days and the curve for the sample C were drawn to guide for eyes.

number of the intrinsic vacancies near the sample surface was smaller when compared with that in the bulk.

To verify this hypothesis, the CsI crystal was washed with water for several seconds, resulting in removing of about 100 μm of the crystal near surface layer. The fresh surface thus created on the crystal was immediately irradiated with the alpha-particle, yielding the emission spectrum shown in Fig. 5c. The observed emission spectrum indicates exactly the same characteristic of the bulk excitation. The peak intensity ratio S/F for the crystal with the fresh layer under alpha-particle excitation is about 1.8 which indeed was in good agreement with that for the bulk excitation.

As described before, intrinsic vacancies could diffuse through the lattice and are annihilated at the surface. The number of the vacancies in the crystal near the surface could, therefore, be less than that in the bulk. On the other hand, as extrinsic vacancies can not diffuse to the surface, an uniform distribution of the extrinsic vacancy should be expected in the crystal volume. If the origin of the slow emission component is related to the intrinsic vacancies, we could expect that the contribution of the slow emission

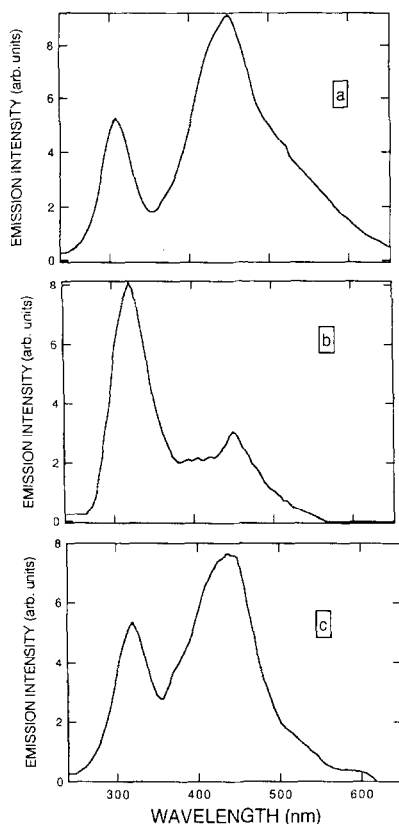


Fig. 5. Emission spectra from the CsI crystal under gamma-ray excitation (a) and under 5.5 MeV alpha-particle excitation (b) and from the same CsI crystal with the freshly exposed surface under alpha-particle excitation (c).

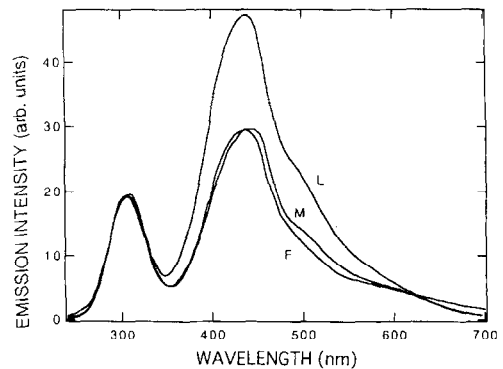


Fig. 6. The emission spectra observed at three different positions (F, M and L) of the crystal under excitation of collimated gamma rays. Here, F, M and L correspond to the first, the middle and the last stage of the crystal growth, respectively.

component in the crystal near surface (i.e. under alpha-particle excitation) be less than that in the bulk (i.e. under gamma-ray excitation). The present results show that this is the case. The increase in the slow emission component for the freshly exposed crystal under alpha-particle excitation can clearly be understood as the result of the appearance of the crystal bulk due to the washing process.

3.3. Intensity variation of the slow emission component for different positions in the crystal

The emission spectra observed at three positions (denoted as F, M and L) of the crystal with 7 cm length under excitation of collimated gamma rays from a RaD–Be source are shown in Fig. 6. The diameter of the collimated gamma rays is about 1 cm. Here, F, M and L correspond to the first, the middle and the last stage of the crystal growth, respectively. The measurement was carried out after three days from the last day of the crystal growth.

The spectra observed show that the intensities of the slow emission component for the positions of F and M are 1.7 times smaller than the intensity of the position L. The positions F and M of the crystal, corresponding to the first and the middle stages of the crystal growth, were submitted to the annealing process for about 35 hours during the crystal growth, while the position L experienced no annealing process. It is therefore natural to expect that the number of the intrinsic vacancies in the positions at F and M be smaller when compared with that in the position L.

Furthermore, the concentration of impurities in the crystal processed by the Bridgman method, in general, is smaller in the first and the middle parts of the crystal compared with that in the last part of the crystal. The number of the intrinsic and the extrinsic vacancies in the positions at F and M is smaller compared with that in the position L. The increase of the relative intensities of the slow component from F to L once more provides an

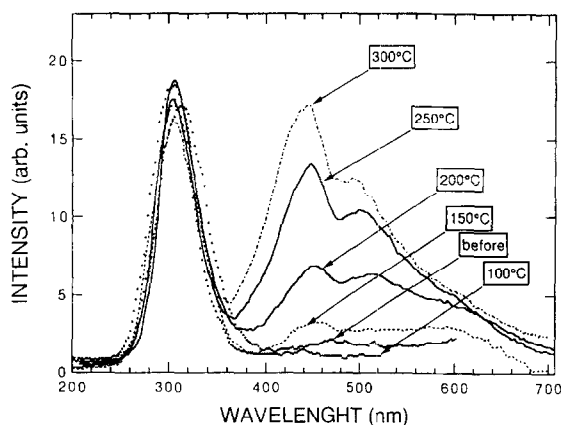


Fig. 7. Emission spectra from the CsI crystal, which was heated to temperatures of 100, 150, 200, 250 and 300°C during one hour, and quenched to room temperature.

indication that the origin of slow luminescence is related to the defects.

4. Thermal quenching

As already described, the initial decrease observed in the S/F ratio of the sample stored at 75°C is more rapid than that at RT. Since the diffusion process of the intrinsic vacancies enhanced at the higher temperature should result in a faster reduction of the number density of the intrinsic vacancies, the annealing process could be considered as a promising way of reducing the slow emission component. However, the number of the intrinsic vacancies is known to increase with increasing temperature as well. Therefore there should exist an optimum temperature at which the annealing for faster suppression of the slow component effectively proceeds, yet the intrinsic vacancies are not significantly increased.

From this view point, sample C was used to search the optimum temperature for the reduction of the slow component. The sample was heated at temperatures of 100, 150, 200, 250 and 300°C for one hour, and quenched to room temperature. After each quenching process, the emission spectrum was measured.

The emission spectra obtained are shown in Fig. 7. The almost complete suppression of the slow emission component was observed at a thermal quenching of 100°C. With the thermal quenching higher than 150°C, the increases in

the intensities of the 450 nm band and the 500 nm were observed. From these observations we could conclude that the optimum temperature for the heat treatment should be around 100°C.

5. Summary

By focusing attention up on the difference in the concentrations of intrinsic vacancies at the different positions of the pure CsI crystal, the emission spectra of the crystal under gamma-ray and alpha-particle excitation were measured. The experimental results seem to provide a strong argument in favor of the intrinsic vacancy model on the origin of the slow emission component. The decrease in the intensity ratio S/F of the crystals 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. The enhancement of the slow emission component is observed at temperatures higher than 150°C.

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