Thermoluminescence from Gamma Irradiated Amino Acids

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Radiation induced thermoluminescence has been studied for five amino acids. The crystalline samples which are pressed to thin disks were irradiated at liquid nitrogen temperature and subsequently warmed to room temperature. Irradiation was carried out by a Co^{60} γ-rays and electron beams from a Van de Graaff accelerator. From glow curves, three conclusions are drawn. (1) Glow curves for phenylalanine, tryptophan, which contain ring structures, have predominant peaks in temperature range 110°K to 120°K with maximum intensity 12 μA. (2) Cystine has such a characteristics but it shows little dose dependency from 10^3 up to 10^7 r. (3) For amino acids except cystine, saturation occurs at about $10^5 \sim 10^6$ r.

INTRODUCTION

As for the radiation damages of macromolecules and organic crystals, only the final states, that is chemical and biological changes, have been studied, and the process by which the substances reach the final changes following the absorption of radiation energy has been inferred only through the observation of the chemical and biological changes But, the techniques such as electron spin resonance began to solve the problem of the intermediate paths by direct measurements. Electron spin resonance can detect the free radicals produced by gamma-irradiation at liquid nitrogen temperature, and in many cases the absorbed energy is stored presumably at these free radicals as well as at lattice imperfections, and impurity atoms.

In general such states of energy storage are metastable and temperature-sensitive. They are stable at low temperature, but become unstable with temperature.

The substances which are irradiated at liquid nitrogen temperature emit light by the subsequent heating. In this socalled thermoluminescence the energy which are stored in the metastable species are transferred some distance and converted to the light quantum. From these considerations, thermoluminescence is another powerful method to investigate the intermediate process, that is 1) transfer of the absorbed energy, 2) localization of the energy at the particular site of molecule, and 3) storage of energy.

Amino acids are the constituent materials of protein and its radiation damage is a fundamental problem to be solved in the radiation biology. Augenstine and his collaborators showed the following results observing the γ-induced thermoluminescence of amino acids[1].

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A) The number of glow peaks is less than three.

B) The peak at 165°K appears in all amino acids.

C) Amino acids with ring structure show a intense peak at 100°K~140°K.

We have also investigated the thermoluminescence of γ-irradiated amino acids, but our main purpose was to see the dose dependency of the glow intensity.

EXPERIMENTAL

Crystalline amino acids were obtained mainly from Nakarai Chemicals. These materials were used without further preparation or purification. A portion of the powdered preparations, 250 mg, was pressed to a disk, 2 cm in diameter. The samples were held at liquid nitrogen temperature while being irradiated with Co^{60} γ-rays, and were heated at a linear rate of 12°K/min from 77°K to about 270°K and the emitted light was measured with a photomultiplier (EMI 9536 B) and a D.C. amplifier. Fig. 1 shows the experimental apparatus. The chromelalumel thermocouple was used to measure the temperature.

The samples were irradiated in the 2000 C Co^{60} γ-rays irradiation facility of the Institute for Chemical Research of Kyoto University. Dose rate was 1.4×10^5 r/h. Irradiation and subsequent heating were made in the atomosphere. In the case of irradiation for the dose above 10^7 r, samples were irradiated by 1.5 Mev electron beam from a Van de Graaff accelerator at Osaka Labpratory of the Japanese Association for Radiation Research on Rolymers were used.

Reproducibility of the glow curve was distorted by the several factors, that is, suppliers of the samples, interval between irradiation and warm up, heating rate, the shape of the samples. Data were reproduced better in high intensity group than in low intensity group.

RESULTS AND DISCUSSIONS

The main data are presented in Table 1. Main glow curves are shown in

Table 1.

No. 1

Amino acid	Dose (r)	Temp. (°K)	Intensity (μA)
Phenylalanine	10^4	117	0.15
		131	0.05
	10^5	123	2.0
	3.6×10^5	113	2.8
		136	1.4
	10^6	133	12.0
	10^7	128	1.3
Tryptophan	10^4	118	0.55
	10^5	112	3.4
	3.6×10^5	102	3.2
		144	2.4
	10^6	116	8.0
	10^7	120	7.0

No. 2

Amino acid	Dose (r)	Temp. (°K)	Intensity (μA)
Methionine	10^4	123	0.05
	10^5	113	0.23
	10^6	117	0.45
		128	0.13
		211	0.038
		101	0.015
	10^7	118	0.19
Lysine	10^5	117	0.0024
		185	0.0015
	3.6×10^5	112	0.003
		195	0.005
		221	0.002
	10^6	129	0.008
		186	0.006
		231	0.003

No. 3

Amino acid	Dose (r)	Temp. (°K)	Intensity (μA)
Lysine	10^7	105	0.0067
		190	0.013
		223	0.012
	10^5	114	0.013
Cystine	3.6×10^5	109	0.0059
	10^6	127	0.012
	10^7	108	0.063

Figs. 2~8. There is some inconsistencys between Augenstine's results and ours. For phenylalanine and tryptophan, there is one prominent peaks at 110°K~120°K, but this peak is divided to two peaks at 3.6×10^5 r. Methionine and lysine have two or three peaks, and cystine has one peaks at 110°K, but its intensity is weaker compared to the amino acids with ring structure. Observations and conclusions are listed in the following.

(1) As mentioned by Augenstine[1], from the peak intensity of glows, we can divide five samples to two groups. Those for phenylalanine, tryptophan, which contain ring structure, have main peaks in temperature range 110°K to 120°K with a maximum intensity of 12 μA. For another group, which contain lysine, methionine, cystine, maximum intensity is the order of 10^{-1}~10^{-3} μA. The intense glow of ring structure amino acids presumably corresponds to the high quantum efficiency of the aromatic hydrocarbons in fluorencese or scintillation.

(2) Dose dependency for five amino acids is presented in Fig. 9. From these dose dependency, we can also divide the samples to two groups. For the samples except cystine, saturation occurs at about 10^5~10^6 r, but for cystine

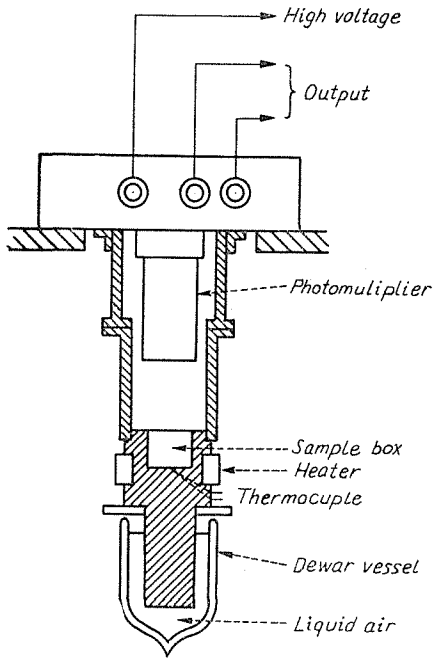

Fig. 1. Experimental apparatus.

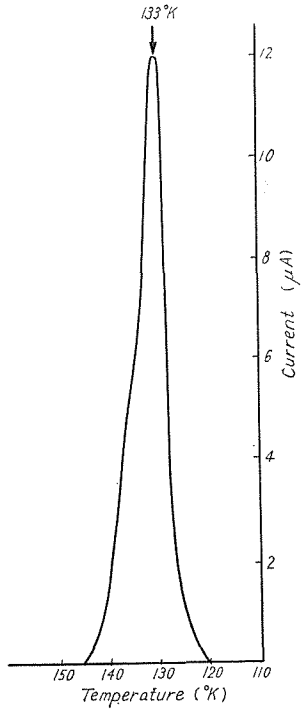

Fig. 2. Phenylalanine, 1×10^6 r.

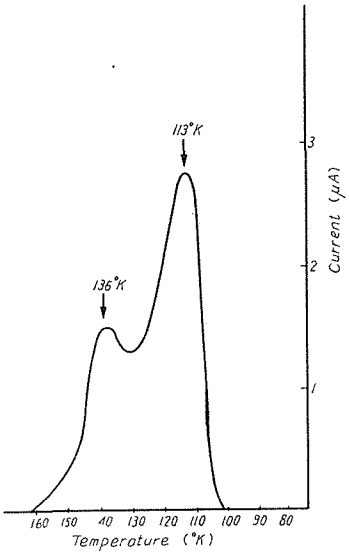

Fig. 3. Phynylalamine, 6×10^5 r.

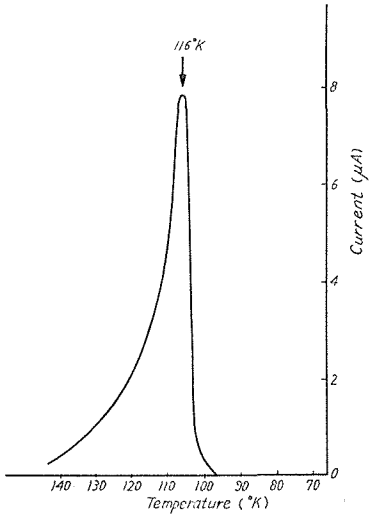

Fig. 4. Tryptophan, 10^6 r.

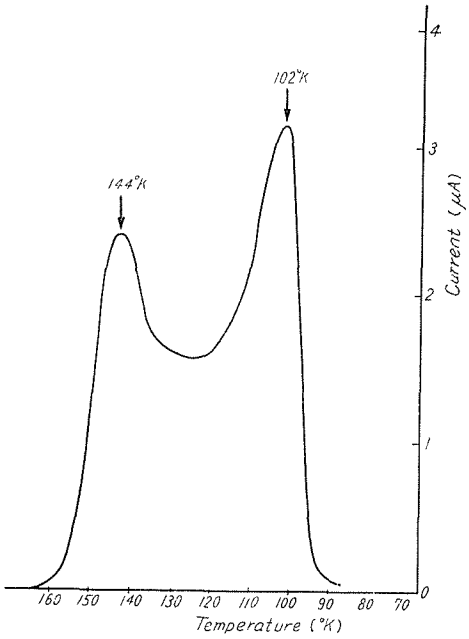

Fig. 5. Tryptophan, 3.6×10^5 r.

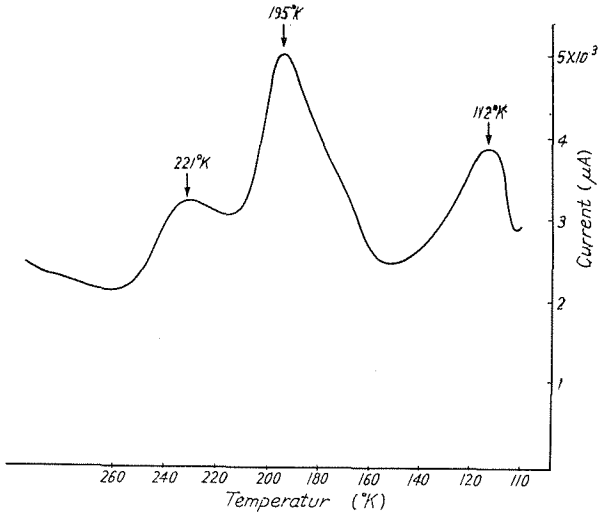

Fig. 6. Lysine, 3.6×10^5 r.

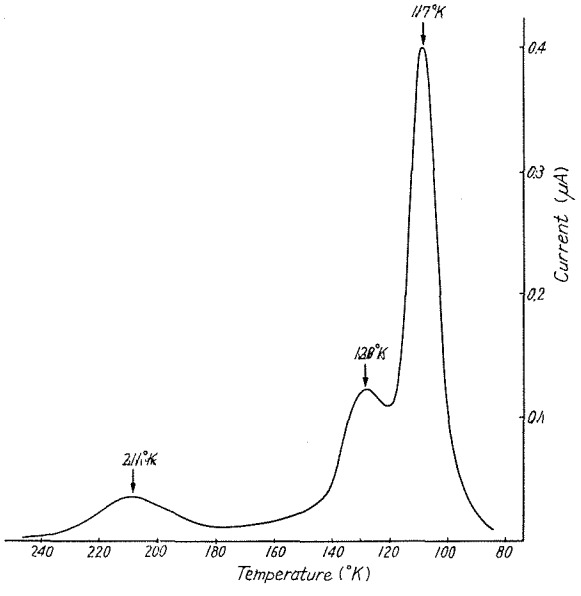

Fig. 7. Methionine, 10^6 r.

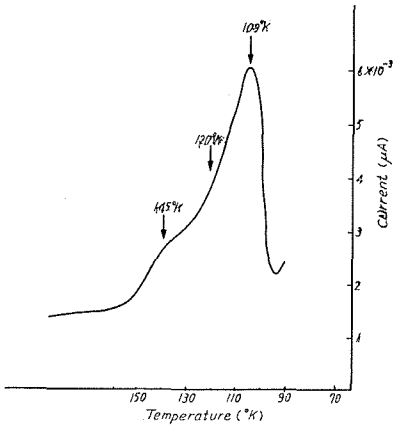

Fig. 8. Cystine, 3.6×10^5 r.

which contains disulphide bonds, prominent dose dependency was not observed within the dose used in this experiment.

The peculiarity of cystine in dose dependency seems to be related to the importance of the disulphide bonds in the inactivation of cystine. Consequently, we can classify five samples to three groups according to the chemical structures.

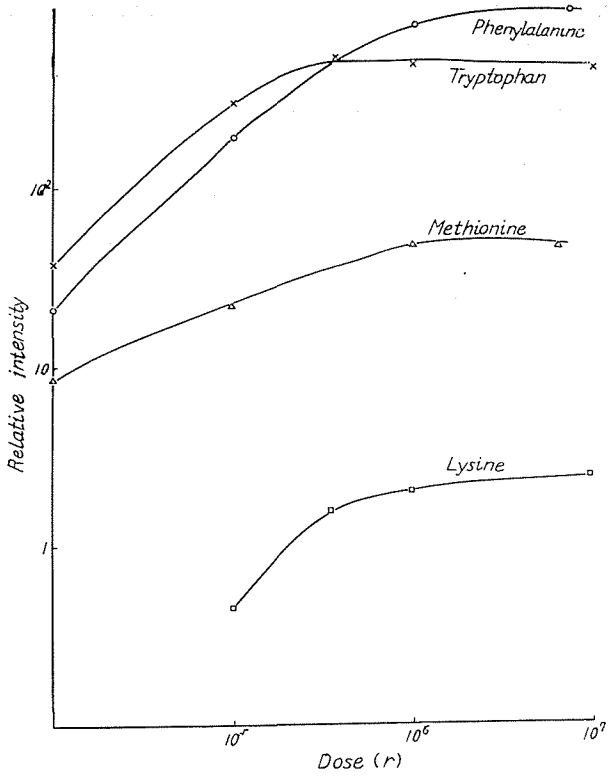

Fig. 9. Dose dependence (amino acids).

This is consistent with the fact[2] that the chemical structure is the important factor in glow curves rather than the crystalline structure. For the result about the dose dependency we can apply the one hit theory in radiation biology and make some order estimation. This theory may be interpreted by the target volume which can be destroyed by one ionization in it. The dose which gives in average one ionization per this target can be calculated from the curve of dose dependency as "37% dose". So, we can calcurate the target volume from the dose dependency. In our case, adopting 10^5 r as the 37% dose, the diameter of the target volume is 300 Å. This order of target volume suggests the existence of some lattice imperfections.

We can not yet derive the decisive conclusions from the above experiment. Together with thermoluminescence, the measurement of conductivity glow are under planning, by which more information seems to be obtained on the trapping states, the carriers of energy etc. Further, it seems nesessary to measure the absorption spectra of the irradiated samples at liquid nitrogen temperature, for there is a fact that the color of the samples by irradiation disappears after the heating.

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