

## Thermoluminescence of $\gamma$ -Irradiated Ruby

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The radiation damages of ruby by gamma ray were studied mainly in regard to its optical properties. By  $\gamma$ -irradiation, some color center is produced in ruby. The damage center has the optical absorption band with its peak at  $465\text{m}\mu$  and is annealed by heating with emission of thermoluminescence. The thermoluminescence occurs in approximately three successive stages, each with its characteristic activation energy. The values of these three activation energies were:  $E_1=0.81\sim 0.85\text{ eV}$ ,  $E_2=0.93\sim 0.94\text{ eV}$  and  $E_3=1.06\sim 1.16\text{ eV}$ . The wave lengths of the thermoluminescence were  $640\sim 680\mu\text{m}$  and  $610\sim 650\text{m}\mu$  corresponding to  $E_1$  and  $E_3$  respectively. The one corresponding to  $E_2$  is not yet observed successfully. As to the intensity of thermoluminescence, it increases with  $\gamma$ -irradiation dose and come to plateau near the point of  $7\times 10^4$  roentgen, whereas it decreases with the concentration of chromium ion. The maximum intensity was observed in the crystal with nominal  $\text{Cr}_2\text{O}_3$  concentration of 0.10%. It seems that, in the mechanism of thermoluminescence in ruby, the initial imperfection of the crystal plays an important role.

### I Introduction

About the radiation damage of ionic crystal many investigations have been reported so far. In connection with the ionic crystal, especially alkali halide irradiated with  $\gamma$ -ray, numerous experimental results about optical absorption spectra, electron spin resonance, electric conductivity, thermoluminescence and so on have been reported and have been explained fairly well.<sup>1)-4)</sup>

When an ionic crystal is exposed to  $\gamma$ -ray, the main effects are considered as follows; in primary process the Compton effect will make the negative ion neutral or excite its electron, and in secondary process, displacement of the neutral atom will take place through the thermal vibration of the crystal lattice. According to Valey's explanation<sup>5)</sup> for the case of alkali halides, a negative ion vacancy will trap an electron, while a positive ion vacancy will capture a neutral alkali metal atom formed during these processes.

When the crystal is composed with multivalent ion, the more complicated mechanisms are expected than in alkali halides. The experimental studies about the radiation damage of these multivalent ionic crystals are carried out by Levy.<sup>6)</sup> He observed an extra absorption band in the visible region (3 eV) in  $\gamma$ -irradiated  $\text{Al}_2\text{O}_3$ , but no explanation was given for the origin of this band.

It has been found that damage centers are produced more easily in the crystal added with the impurity ion of different valence from the host. This is because of the increased imperfections of the crystal. In the case of ruby the radiation effect seems to be much different from that of  $\text{Al}_2\text{O}_3$ , probably because the presence of the impurity affects the phenomenon seriously.

In this paper, are presented several experimental results about the thermoluminescence of  $\gamma$ -irradiated ruby; in particular, the variation of the wave length and the intensity of thermoluminescence spectrum, corresponding to the variation of irradiation dose or the chromium concentration.

The activation energies for glow emission are determined experimentally for each case.

### II Experimentals

#### II-1) Sample

The ruby crystals used were obtained from the Shinkō-sha Co. (Japan) and grown by the Verneil process. The characteristics of the samples are listed in Table I. Since  $\text{Cr}_2\text{O}_3$  added in  $\text{Al}_2\text{O}_3$  vaporizes during the course of crystal growth, its final concentration is smaller than added. Generally, the tri-valent chromium ion is considered to be distributed homogeneously in the crystal. But it became evident as the result of micro-optical examination<sup>10)</sup>

that  $\text{Cr}^{+++}$  ions are distributed more near the surface of a crystal than interior.

Table I. The characteristics of samples.

No.	$\text{Cr}_2\text{O}_3$ Nominal conc.	$\text{Cr}_2\text{O}_3^*$ conc. in boule	
1	0 %	0 %	Sapphire
2	0.05	0.03	Size; $10 \times 7 \times 3$ mm
3	0.10	0.06	
4	0.50	0.25	All samples contain their C-axis in the largest plane.
5	1.00	0.48	
6	3.00	1.20	

\* By chemical analysis.

In this experiment were used comparatively homogeneous crystals which were cut out of the interior of the boule.

### II-2) Apparatus

The apparatus shown in Fig. 1 was used to observe the spectrum of thermoluminescence corresponding to glow peak. All absorption measurements were made with a Hitachi-EP5-II recording spectrophotometer.

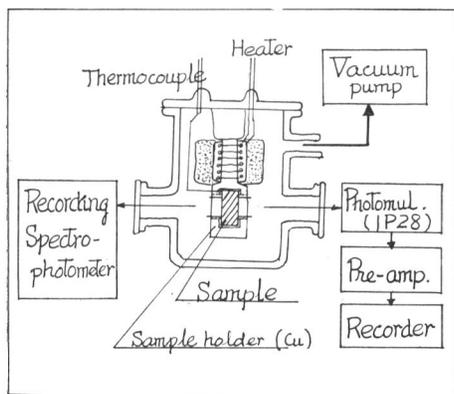


Fig. 1. Block diagram of apparatus.

### II-3) Procedure

The samples were irradiated with 3000 curie  $\text{Co}^{60}$  (as the  $\gamma$ -source) at the dose rate of  $2 \times 10^5$  roentgen/hr. After irradiation, the ruby was heated on an electric heater at the rate of warming of  $0.4^\circ\text{C}/\text{sec}$ . Consequently, temperature of the sample rose about  $4^\circ\text{C}$  during the time for scanning over the necessary wave length region ( $500 \sim 800\text{m}\mu$ ). Both the measurements of thermoluminescence spectra and the glow intensity were carried out at the same time.

## III Results

### III-1) Absorption Spectrum

A new absorption band appears in ruby after irradiation by  $\gamma$ -ray as shown in Fig. 2 and Fig. 3. This additional absorption has its peak at  $465\text{m}\mu$ , and its intensity increases with the irradiation dosage until it saturates at around  $4 \times 10^6\text{r}$ .

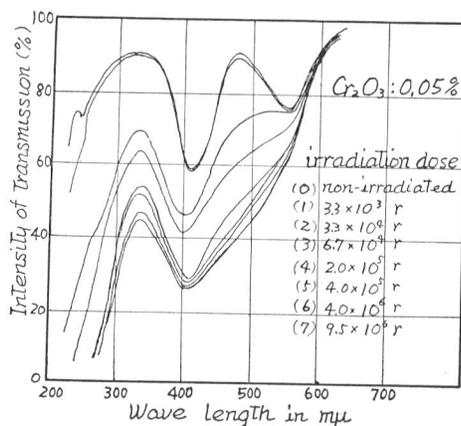


Fig. 2. Dose dependence of absorption spectrum.

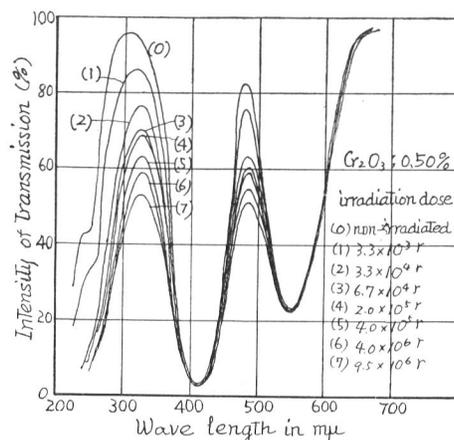


Fig. 3. Dose dependence of absorption spectrum.

According to Levy, a pure  $\text{Al}_2\text{O}_3$  crystal shows, after  $\gamma$ -irradiation, a very broad absorption with the peak at  $400\text{m}\mu$ . But its intensity does not increase beyond certain low level even after the prolonged irradiation, and so, may be considered to have an entirely different origin from the extra absorption of ruby. In fact, the intensity of the new absorption shows a strong dependence upon the Cr concentration, and this fact suggests the important role of Cr ion in the coloration.

Little shift was observed of the new absorption band by varying the Cr concentration.

Provided that Smakula's formula may be applied to the case under consideration, the concentration of the color center ( $N_c$ ) can be estimated from the observed half-width and the assumed value of the oscillator strength ( $f$ ):

$$N_c f = 1 \times 10^{16} \text{cm}^{-3} \text{ for the sample of } 0.05\% \text{ Cr concentration with the total dose of } 2.8 \times 10^6 \text{r.}$$

For  $f=0.1$ ,  $N_c=1 \times 10^{17} \text{cm}^{-3}$ , or about 1 color center per 100 Cr ions. This result can not be taken literally, but seems to fall within the reasonable range of magnitude.

III-2) Glow characteristics

When heated, the irradiated crystal was found to display thermoluminescence, while the new absorption band mentioned above, disappears on cooling down to the room temperature. The glow characteristics for various radiation dosage and the Cr concentration are shown in Fig. 4 and 5, respectively. As can be seen there, the glow emission occurs apparently in three successive stages, their relative intensity changing with the variation of the Cr concentration.

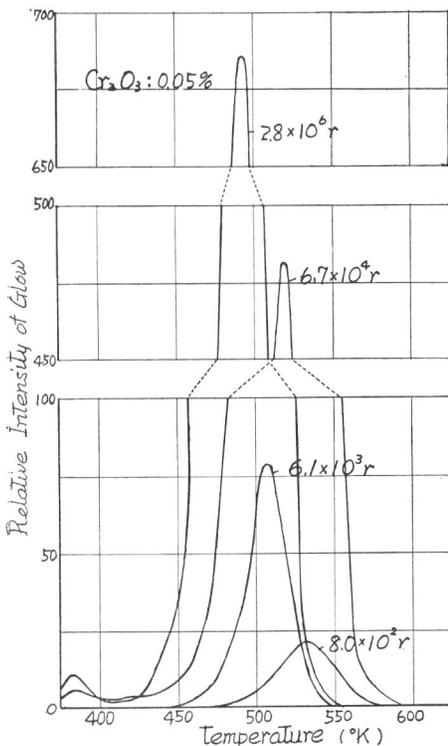


Fig. 4. Dose dependence of glow.

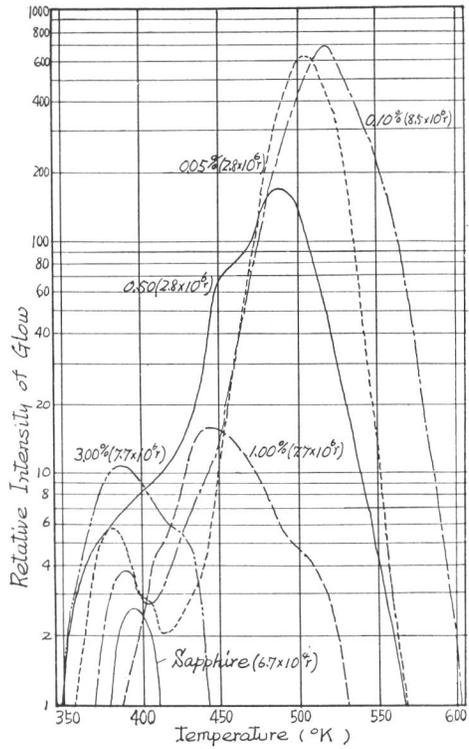


Fig. 5. Cr-concentration dependence of glow.

These three components may be designated as I, II, and III, respectively, with increasing order of temperature.

The emission spectra of the component I and III are reproduced in Figs. 6 and 7, respectively. In common to both, the emission peaks shift toward the high frequency as the decay proceeds. This phenomenon of blue shift is found dependent of neither the

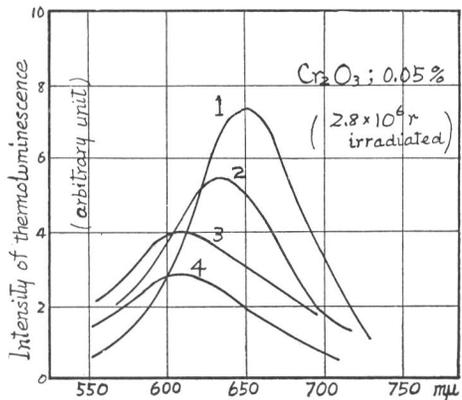


Fig. 6. Spectrum of thermoluminescence. The spectrum was observed successively in the order of curve 1, 2, 3 and 4 with the interval of 45 sec between each run.

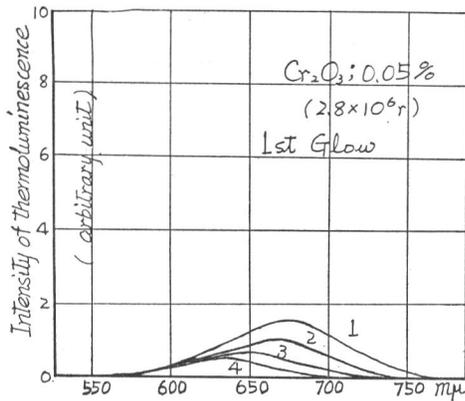


Fig. 7. Spectrum of thermoluminescence. The spectrum was observed successively in the order of the curve 1, 2, 3 and 4 with the interval of 45 sec between each run.

irradiation dosage nor the Cr concentration.

It may be explained as the result of temperature elevation. The observation of the emission spectrum of the component II has been unsuccessful so far.

If it is assumed that each of the three glow components is independent process with its own activation energy, the method by Randall and Wilkins<sup>7)</sup> can be applied to calculate the activation energy  $E_{I, II}$  or  $III$  from the observed glow characteristics. It is expressed as

$$E = kT_m \left( 1 + \ln \frac{kT_m^2}{E\beta} / \ln s \right) \cdot \ln s$$

where,  $k$  is the Boltzmann constant,  $T_m$  the temperature of the glow peak,  $\beta$  the rate of warming and  $s$  can be determined experimentally.<sup>8)</sup> In Table II are listed the activation energies estimated for some of the samples studied.

Table II. Activation energy

No.	Concentration of $\text{Cr}_2\text{O}_3$ (nominal)	Irradiation does (roentgen)	Activation energy in eV		
			1 st Group	2 nd Group	3 rd Group
1	O(Sapphire)	$6.7 \times 10^4$	0.83		
2	0.05%	$8.0 \times 10^2$			1.16
		$6.1 \times 10^3$			1.10
		$6.7 \times 10^4$	0.81		1.13
		$2.8 \times 10^6$	0.81		1.07
3	0.10%	$8.5 \times 10^6$	0.82		1.11
4	0.50%	$2.8 \times 10^6$		0.93	1.06
5	1.00%	$7.7 \times 10^6$	0.85	0.93	
6	3.00%	$7.7 \times 10^6$	0.82	0.94	

### III-3) Correlation

The relationship observed between the glow emission and absorption may be summarized as follows. The absorption band with its peak at  $465\text{m}\mu$  disappears after glow emission.

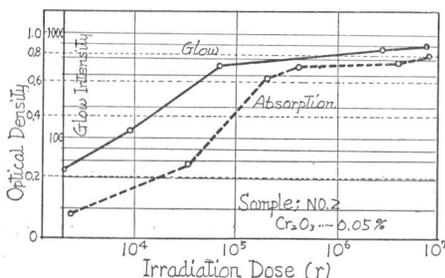


Fig. 8. Correlation of glow and absorption intensity

Moreover, as is shown in Fig. 8 the glow intensity and absorption intensity show the similar dependence on the irradiation dosage in the range of  $10^3 \sim 10^5$  roentgen. From these experimental results, the damage center which caused the glow emission may also take an essential part in originating the new absorption.

### IV Discussion

Before discussing the glow mechanism, the initial properties of the crystal before irradiation must be considered. As indicated in Table I the concentration of chromium in boule is about 60 per cent or less of the nominal quantity. Moreover, the concentration of  $\text{Cr}^{3+}$  ion is predicted to be less than the whole concentration in a boule from the

measurement of susceptibility and E. S. R. This fact indicates that some of the tri-valent chromium ion would change its valence in the process of crystal growth and it will stay in the crystal in the form of  $\text{Cr}^{2+}$ ,  $\text{Cr}^{4+}$  or  $\text{Cr}^{6+}$  ion.

This possibility should naturally be taken into account in discussing the imperfection of the crystal, since these different chromium ions will affect the crystal seriously. For example, the presence of  $\text{Cr}^{2+}$  ion will cause the production of negative ion vacancy near itself and  $\text{Cr}^{4+}$  or  $\text{Cr}^{6+}$ , the positive ion vacancy in the same manner. As the temperature is sufficiently high (above  $2000^\circ\text{C}$ ) during the crystal growth, the presence of  $\text{Cr}^{4+}$  or  $\text{Cr}^{6+}$  is easier to assume since  $\text{Cr}^{2+}$  ion will be relatively unstable at elevated temperature.

If the initial properties of ruby is assumed as mentioned above, it seems possible to consider a model for the irradiation effect and the thermoluminescence observed.

Suppose an oxygen ion is doubly ionized with  $\gamma$ -irradiation and the positive holes are formed on it. These positive holes may migrate in the crystal at room temperature. Then they will be trapped around a positive ion vacancy which is present initially. This center may be something like  $V_1$ -center proposed by Seitz<sup>9</sup> except that two holes be trapped in this case. Two electrons released from an oxygen ion will be trapped at the negative ion vacancy which is present initially at the relatively small ratio to the positive ion vacancy. The electrons in the trap will make a singlet state and will originate the extra absorption band after  $\gamma$ -irradiation.

The glow emission will occur when the positive holes of  $V$ -like center recombine with the trapped electrons by heating. In the recombination process, two models may be possible.

If the electron capture cross section are equal among all the emission center as assumed by Randall and Wilkins, three kinds of activation energies may be presented corresponding to each glow peak. The presence of three kinds of activation energy may be interpreted as follows: The amount of energy required for releasing holes thermally will depend on the type and strength of the

crystalline field in which each hole is trapped. As described before, the positive ion vacancy is made probably near the lattice point of  $\text{Cr}^{4+}$  ion. The relative positions of  $\text{Cr}^{4+}$  ion and the vacancy regarding the crystalline axis are possible in several ways. Corresponding to each configurations, the potential of vacancy will be varied, causing three different activation processes.

On the other hand, if the electrons trapped in the negative ion vacancy are more mobile, they will be released with only one activation energy and will fall into the positive ion vacancy trapping positive holes which have three different electron capture cross sections corresponding to three glow peaks. And in this case, the presence of three kinds of cross sections may also be explained with the variation of the configurations mentioned above.

Needless to say, the explanations given above are among a few possibilities and must be corrected by the future investigations.

In conclusion, it can be said that the main stage in the thermoluminescence in the  $\gamma$ -irradiated ruby have been determined. The mechanisms involved in the glow process are yet to be investigated.

#### Acknowledgement

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## DISCUSSION

**Iida, Y.:** I want to ask you two questions about experimental procedures. (1) Was the measurement of the optical absorption made parallel or perpendicular to the C axis? (2) Did you make some reducing heat treatment of crystals, or did you use the boules as grown?

**Maruyama, T.:** (1) We performed the optical absorption measurements perpendicular to C axis. (2) About the heat treatment, we did not make it. And we are not sure whether the supplier of the crystal made the heat treatment or not.

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## Luminescence of Doped Silver Chloride with Divalent Anions and Cations

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Several luminescence maxima of doped silver chloride crystals are obtained spectroscopically. Some of the peaks are common to more than two impurities. The peak at 520 millimicron appears with some divalent anion impurities. The peak at 545 millimicron does with some divalent cation impurities, and peaks at 485 millimicron do with both of the impurities.

Infrared quenching of the luminescence and photoconductivity at 1000c/s is measured simultaneously. It is inferred by calculation that the peaks at 485 millimicron and 520 millimicron are hole type luminescence and the peak at 545 millimicron electron type one.

Those peaks are attributed to the defects proper to silver chloride crystals which can be introduced by the impurities, *i.e.* silver vacancies are responsible for the peak at 545 millimicron and interstitial silver ions or halogen vacancies for the peak at 520 millimicron. As to the peak at 620 millimicron thermally decomposed silver atoms are responsible, and the peak at 485 millimicron may be due to the electron shallow traps accompanying other defects such as dislocations.

Doped crystals of silver chloride are obtained by Kyropoulos method with impurities of  $10^{-5}$ – $10^{-3}$  in mol ratio of  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_2\text{Se}$ ,  $\text{Ag}_2\text{Te}$ ,  $\text{CdCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{PbCl}_2$  and especially  $\text{FeCl}_3$  added into the melt respectively. Many other impurities are also examined. Luminescence of these crystals is measured spectroscopically at temperatures from liquid nitrogen to room temperature. Infrared quenching and thermal quenching of the luminescence are obtained. Photoconductivity of the crystals at 1000 c/s is measured simultaneously with the luminescence, and the both are recorded. A brief result is shown in Fig. 1.

Since most of the intensity maxima of the luminescence spectra are common to more than two impurities, these peaks are attributed to defects proper to silver chloride instead of proper to impurities. For example, a peak at 485 millimicron which appears in the purest samples also appears in the crystals containing O, Se, Cd, Pb and Fe. A peak at 545 millimicron appears in the crystals containing Cd, Ca and Pb, and that at 520 millimicron does as to S, Se and Te. A peak at 620 millimicron (remarkably suppressed by the photomultiplier characteristics on recording paper for longer wave length than about 580 millimicron) appears in the crystals containing O, Se and Fe.