主論文

Strain-Stimulated Luminescence: A Detection for Marble and Mechanism Inferred from Thermally Stimulated Luminescence

歪刺激ルミネッセンス：大理石における検出と熱刺激ルミネッセンスを用いたメカニズムの推定

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Strain-Stimulated Luminescence: A Detection for Marble and Mechanism Inferred from Thermally Stimulated Luminescence

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1.Introduction

Various kinds of light emission have been reported associated with earthquakes known as Earthquake light (EQL). In smaller scale, the luminous phenomena have been also reported at the rock burst in mine. These phenomena are of interest in viewpoint of the prediction of earthquakes or rock bursts and prevention of hazard. Derr[1] reviewed the observations of EQL and possible mechanims. Some mechanisms of EQL have been proposed, i.e., discharge due to electrical potential gradient produced by piezoelectricity or stream potential of ground water flow[2)-6)], excitation of ambient atmosphere by exoelectron[7] and sonoluminescence in water[8]. There are few studies, however, which confirmed the occurrence of the phenomena by laboratory experiments. At the present stage, it needs to examine the possibilities of all the proposed models in laboratory experiments.

Brady and Rowell[7] carried out the experimental studies on the luminescence at the fracture of rocks. They observed the spectrum of the light emitted from the rocks and they found that the spectrum consists of the lines of the ambient atmospheric atoms.

They concluded that the light was due to the excitation of the atmospheric atoms by exoelectron emitted from the rock specimen at fracture. The fracture experiments were done in a condition of quite high strain rate and the fracture was explosive. Therefore, they could not observe the light emission as a precursory phenomenon of the fracture. It is of interest to test the occurrence of the light emission at loading in lower strain rate and before failure.

In the fields of solid state physics, many authors have tried to observe light emission at loading and fracturing solid specimen in laboratory experiments (see a review by Walton[9)]). Photon emission associated with the recombination of electrons and holes previously trapped at point defects is one of the well-documented phenomena in deformation luminescence of alkali halides[10)-13)]. When a solid specimen is irradiated, the point defects trap the excited electrons and holes. The trapped electrons and holes would be liberated when consuming a part of the strain energy under stress. This process is analogous to thermally stimulated luminescence (TSL) or optically stimulated luminescence (OSL). Thermal or optical energy supplies the energy to liberate the electrons and holes. In this paper, the term "strain-stimulated luminescence (SSL)" is used as the luminuous phenomenon induced by the recombination of previously trapped electrons and holes under stress. Although there are various mechanisms of luminescence under stress and at fracture, SSL is distinguishable among them by evaluating the effect of irradiation on luminescence, i.e., SSL occurs only when the sample is previously irradiated. In crustal rocks, electrons and holes have accumulated at traps because of natural irradiation by radioactive elements in rocks. Therefore, one can expect SSL associated with earthquakes or rock bursts.

The first purpose of this paper is to examine whether SSL occurs or not when loading ordinary crustal rocks. The occurrence of the phenomenon has been well established for the samples of Alkali halides single crystal. They deform in ductile manner under even room temperature and the movement of dislocation strongly relates with the photon emission[10)–13)]. In contrast, crustal rocks are generally pollycrystalline solids and show brittle behavior under uniaxial stress. There are no reports that specify the mechanism of luminous phenomenon at loading and fracturing crustal rocks as to be electron and hole recombination.

Thermally stimulated luminescence (TSL) gives us some insights about the structure of trapping sites and the amount of trapped electrons and holes. If application of stress strongly affects the trapping sites, TSL can detect any change of trapping sites. It is the second purpose of this paper to illustrate a feasibility of TSL method to investigate microscopic behavior of solid at deformation and fracture. I tried to detect any change in TSL spectrum before and after the loading and discuss its relation with SSL.

We can apply the luminous phenomena, when their mechanisms become clear, to the predictions of earthquake or rock burst. The third purpose of this paper is to propose a new method for the prediction of rock bursts in mine based on the results of this experimental study.

2. Experimental Procedure

The specimen used here is the Akiyoshidai marble, which consists of fine calcite with little accessory minerals. Marble is the simplest rock in the viewpoint of mineral composition among crustal rocks. Therefore, it is favorable for our first attempt to detect light emission under stress and to specify its mechanism. I prepared two types of samples, i.e., for loading experiment and for TSL measurement. For loading experiment, the specimen was cut into cylindrical shape with 25 mm in length and 25 mm in diameter, and then washed and dried. Another part of the same specimen block was crushed into powder with hammer mil for preparing TSL sample. Fine grain (smaller than 0.1 mm) was sieved out.

I tried to observe the photon emission at loading the sample that had been previously irradiated and the change in TSL spectrum before and after the loading and fracturing. Both loading sample and TSL sample were exposed by ^{60}Co gamma ray in dose rate of 162 Gy/hour for three hours. The powder sample is set into a pair of acrylic resin plate with thickness of 4mm in order to equalize secondary electron flux to intact solid of the loading sample. We consider the irradiated powder sample as "before loading" sample in viewpoint of TSL spectrum change. The samples were annealed at room temperature for two or three weeks until gamma afterglow became sufficiently weak to observe photon emission at loading.

Figure 1 shows the schematic constitution of the loading experiment. A servo-controlled loading apparatus applied the uniaxial stress to the sample in constant-strain-rate mode. The runs were carried out in three different strain rates as 5.0×10^{-5} ,1.0×10^{-4} and $2.0 \times 10^{-4} sec^{-1}$. A loadcell settled in the ram measures the applied load and axial compression stress is calculated from the load divided by the area of the endplane of the sample. Acoustic emission (AE) activity was also observed with a

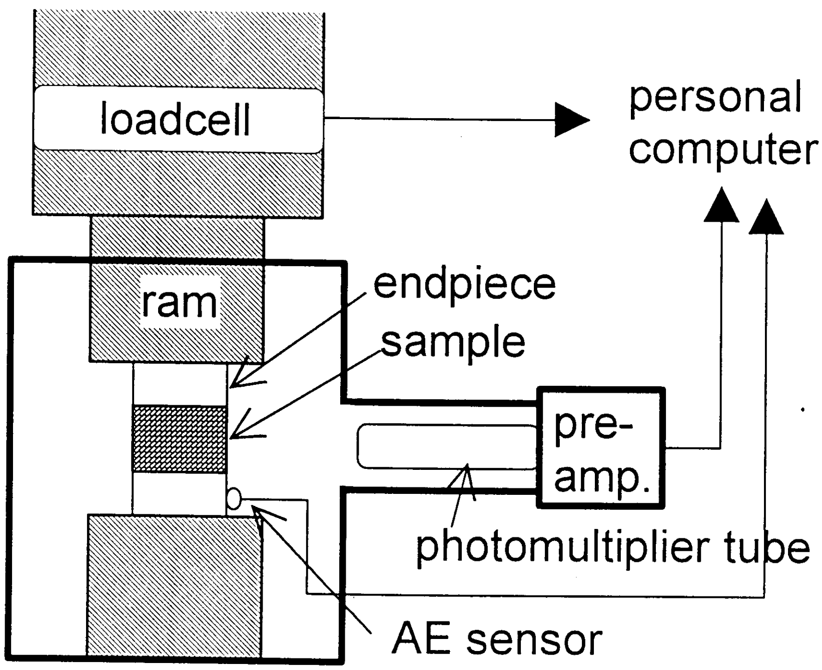

Figure 1. Schematic figure of loading experiment. A personal computer records the output of loadcell. Both the output pulses of photomultiplier tube and acoustic emission (AE) sensor are counted and recorded by the personal computer.

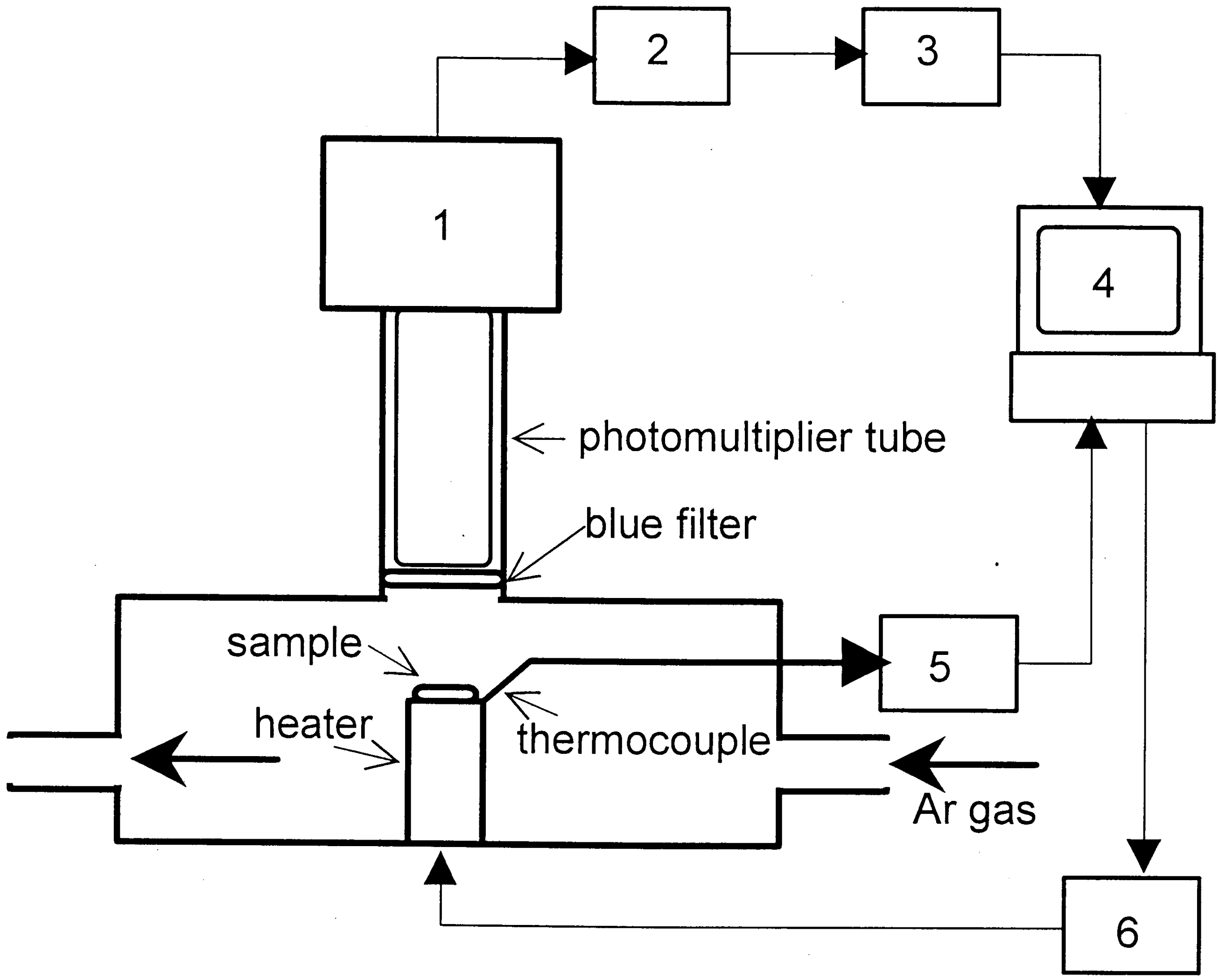

Figure 2. Schematic figure of TSL experiment. 1: preamplifier of photomultiplier tube, 2: discriminator, 3: counter, 4: personal computer, 5: thermocouple amplifier and 6: power controller for the heater.

piezoelectric sensor attached on the side wall of an endpiece by counting ultrasonic wave pulses whose amplitude was larger than a given threshold.

The photon emission during the loading was observed with a photomultiplier tube facing to the side wall of the sample. The photomultiplier was Hamamatsu Phtonics' type R268 that has a sensitivity for near UV to orange with peak at 400 nm. A counter counts the photo-electrical pulses for every one second and the numerical data is recorded by a personal computer.

The fragments of fractured sample were sieved to get particles as fine as the TSL sample. I then measured the TSL spectrum as "after loading" samples. Note that this specimen of "after loading" is a group of the finest fragments of fractured sample so that it must be most severely suffered the effect of loading and fracturing on the traps of electrons and holes. Just after the SSL experiment, I measured the TSL spectrum of both "before loading" and "after loading" sample. Figure 2 is a schematic figure of TSL measurement. Sample was weighed around 10 mg for each measurement and the photon emission intensity was normalized as expected for just 10.0mg of the sample. The heating rate was 0.3 K/sec and a photomultiplier tube counted the photon emission. The photomultiplier tube was Hamamatsu Photonics' type R1282, which was designed for the usage in high temperature environment and has a sensitivity for near UV to orange with peak sensitivity at 370 nm. I used blue filter (Kenko B-410, 50% cutoff at 500 nm) to cut thermal radiation. Argon gas was filled heating chamber to avoid any chemical reaction of the sample with air under high temperature.

3. Results

1) TSL spectra

Figure 3 shows the TSL spectrum of the specimen and its growth with gamma dose. Horizontal axis is temperature and the vertical is photon counting rate in unit of 10^3 counts per second. The sample with no irradiation shows also a TSL peak at 440K and a small shoulder at 500K. This shows that electrons and holes had accumulated at some trapping sites by irradiation of natural radioactivity.

A peak at 390K appears by artificial irradiation and the peaks at 440K and 500K also grow with gamma dose. Thus, the specimen includes at least three trapping sites. Medlin[14)] investigated TSL of natural calcite and reported the peaks at 350K, 500K, 600K and 700K. He concluded that the specimen includes at least four electron trapping sites and one hole trapping site. The luminescence occurs by exciting Mn^{2+} ion. The peak at 390K observed here may be the same one at 350K by Medlin (1964); the sift of peak temperature can be attributed to room temperature annealing in this study. The peak at 500K must be the same one reported by Medlin, whereas the peak at 440K is left unspecified. The sample used here does not show the TSL peak at 600K, and the current measurement cannot observe the peak at 700K because of the superimposition of thermal radiation.

2) Photon emission at loading

Figure 4 exhibits a result of loading experiment. The top of the figure shows the temporal change in stress and AE activity and the bottom that in photon emission. The sample had been irradiated for 480 Gy and left in room temperature for 24 days. Strain rate was $2.0 \times 10^{-4} sec^{-1}$. Since the strain rate was kept constant, one can see the stress variation with time as a stress-strain relation. The stiffness of the loading apparatus is high enough to obtain a complete stress-strain diagram. The failure of the sample is not

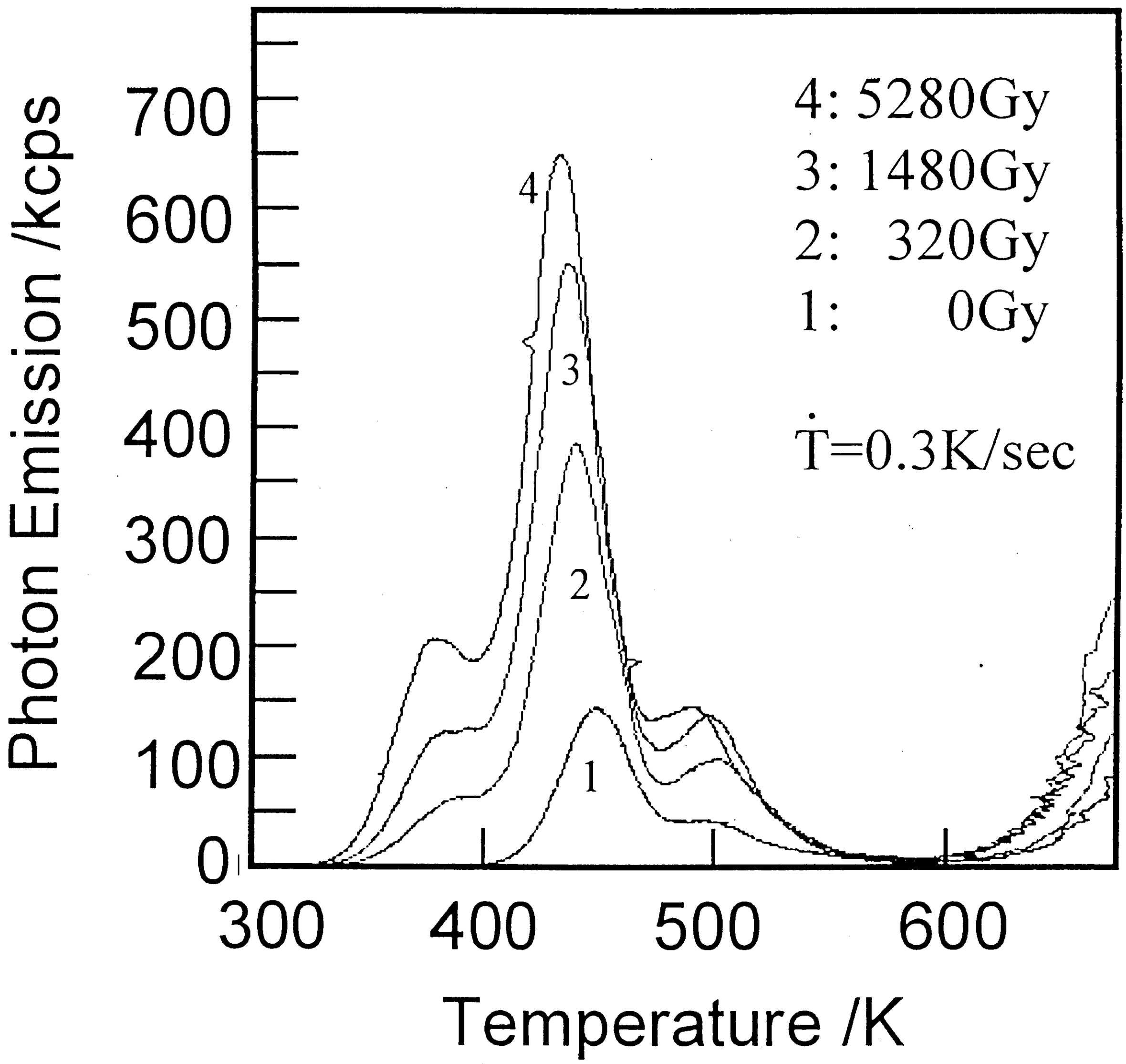

Figure 3. The TSL spectrum of the Akiyoshidai marble. Horizontal axis is temperature and the vertical is the poton counting rate in unit of 10^3 counts per second. Irradiated gamma dose is shown for each curve. Heating rate was 0.3 K/sec. The TSL mesurements were carried out 15 days after the irradiation.

explosive. In every experimental run the sample fractured by several vertical fracture planes. The fracture planes appear on the side surface of the sample just before the stress reaches the maximun value, when AE becomes active. The sample fractured into several relatively large pieces.

As shown in the lower portion of the Figure 4, photon emission was detected for irradiated sample. Back grounds of photon count were 6.1 counts per second as average over one thousand seconds before loading and its standard deviation was 4.8 cps. The bold broken line shows the average back ground and the thin the level of one standard deviation above the average. Almost of the background photon counts are due to gamma afterglow. The maximum intensity of photon emission was more than 7 times of the background. It should be noted that the emission attained the maximum intensity before the AE became active; photon emission seems to relate with not AE activity but with stress.

Figure 5. shows temporal change in stress, AE activity and photon emission for non irradiated sample. The strain rate is the same as the run of irradiated sample shown in Figure 4. In contrast to irradiated sample, there are no photon emissions at loading. This indicates that the photon emission detected for irradiated sample directly concerns with gamma irradiation, so that, one can say that the photon emission shown in Figure 4 is strain-stimulated luminescence. This is the first conclusive report of the luminous phenomenon at loading of crustal rock through the mechanism of recombination of trapped electrons and holes.

TSL intensity increases as heating rate dose because the total number of photons emitted depends on the sum of the number of electron-hole pairs previously trapped and it is the same for any heating rate, whereas, the intensity is measured by the number of photon emitted in unit time. One can expect for strain rate to have similar effect on SSL

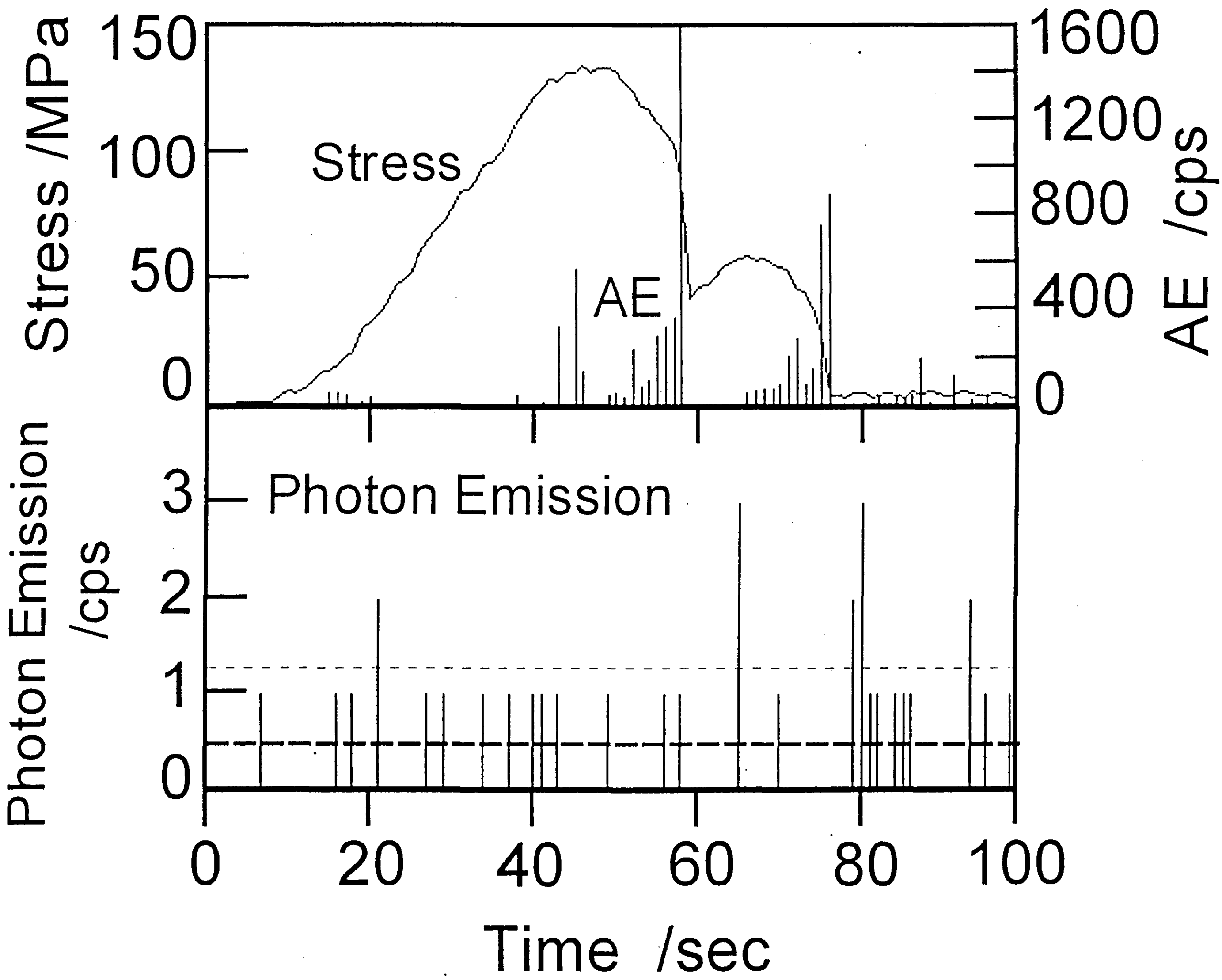

Figure 5. A result of loading experiment for non irradiated sample. Strain rate was $2.0 \times 10^{-4} sec^{-1}$. The upper portion of the figure shows the temporal change in stress and AE activity. The lower shows the temporal change in photon emission intensity. The back ground photon count is 0.47 cps averaged over one thousand seconds before the loading and it is shown by bold broken line. The level one standard deviation (0.33 cps) above the average is also shown by thin broken line.

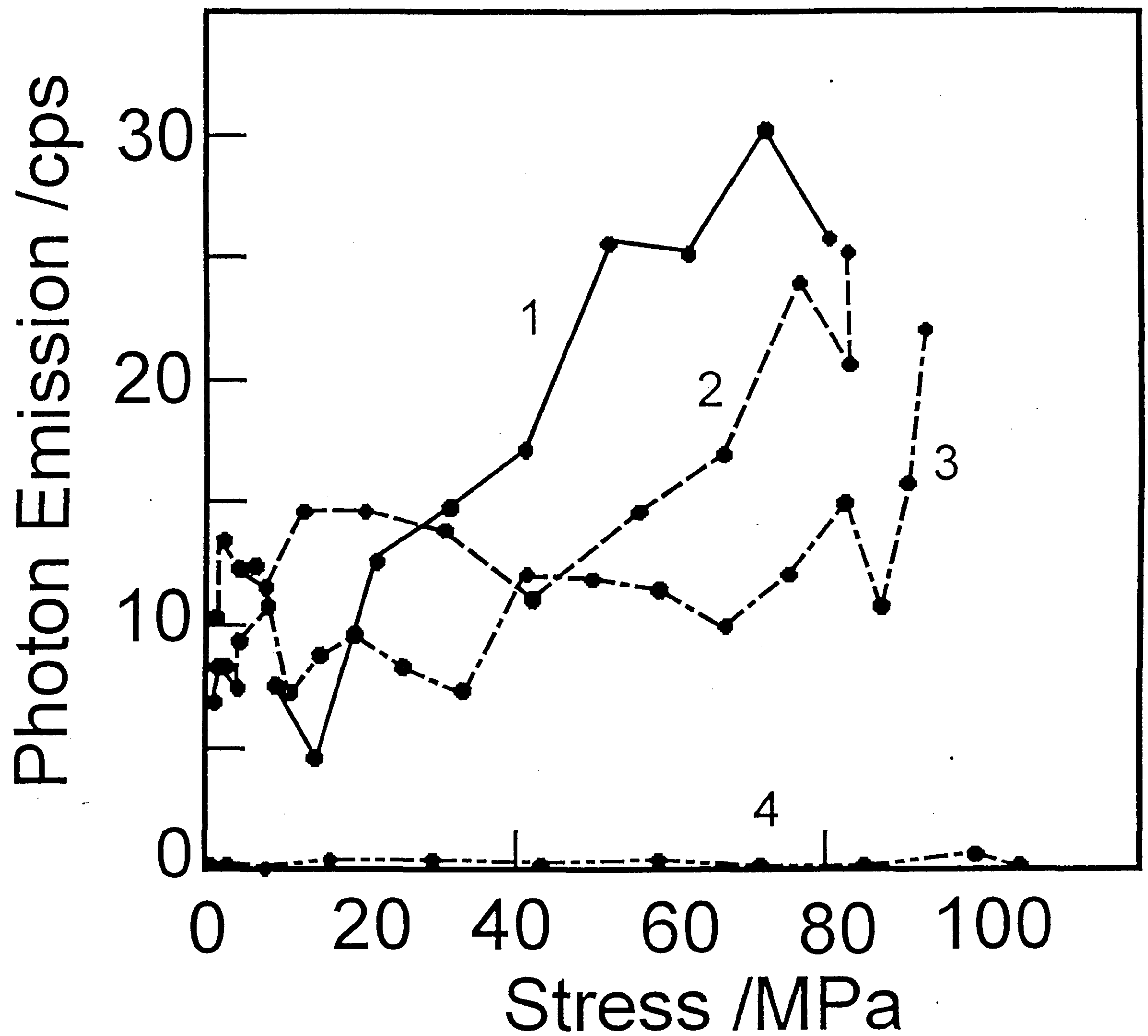

Figure 6. The relationship of photon emission intensiy with stress up to the maximum stress. Irradiated gamma dose and strain rate are as follows; 1: 480 Gy, $2.0 \times 10^{-4} sec^{-1}$, 2: 490 Gy, $1.0 \times 10^{-4} sec^{-1}$, 3: 490 Gy, $5.0 \times 10^{-5} sec^{-1}$ and 4: 0 Gy, $2.0 \times 10^{-4} sec^{-1}$. The dot denotes the value averaged over every 4 seconds for the run with strain rate of $2.0 \times 10^{-4} sec^{-1}$ and 10 seconds for the others.

intensity. Figure 6 plots the SSL intensity against stress up to the maximum stress for three different strain rates. The photon emission intensity increases as stress increases, and, as expected, the higher strain rate gives the stronger photon emission. Figure 6 also shows the contrast between the irradiated sample (curve 1) and the non irradiated (curve 4) under the same condition of strain rate. Clearly the irradiation activated the photon emission at loading.

3) Change in TSL spectrum before and after the loading.

Figure 7 shows the TSL spectra of the non irradiated specimen. Comparing the spectrum after the loading with before loading, the peak at 440K was unchanged, whereas the peak at 540K appeared after the loading. Since the specimens here had not been irradiated, difference of two samples is only at the mode of fracture. "Before" loading sample was crushed with a hammer mil and "after" loading sample was fragment by static loading. The change in the TSL spectra means that TSL peak at 540K is due to the loading itself. It is left for future study to specify the structure of this trapping site and the mechanism to create it through loading. Neverthless, the appearance of new TSL peak shows a potential feasibility of TSL method as a tool for specification of microscopic processes of deformation and fracture. This also implies a possibility to read out the history of the loading or stress state from the crustal rocks with TSL method.

Figure 8 shows the change in TSL spectrum "before" and "after" loading for irradiated sample. The sample suffered 490 Gy gamma irradiation and was loaded with strain rate of $5.0 \times 10^{-5} sec^{-1}$. As clearly shown, the peak at 390K decreased, the peak at 440K left unchanged and a peak at 540K appeared. The sample loaded with strain rate of $2.0 \times 10^{-4} sec^{-1}$ shows the same feature in TSL spectrum change (Figure 9). This tendency was seen in all the samples.

Table 1 lists the integrated TSL intensity for each peak that must be proportional

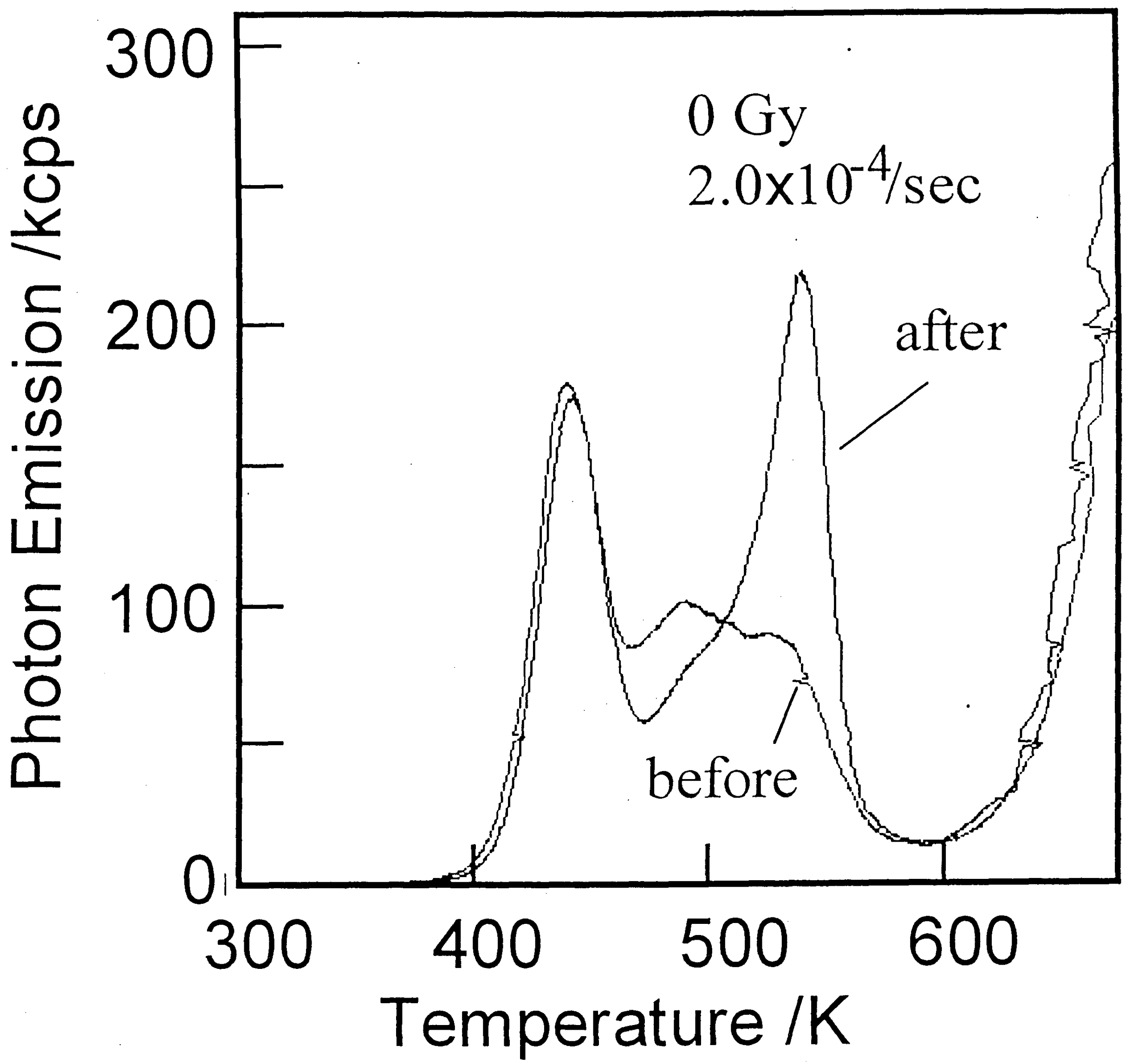

Figure 7. TSL spectra of "before loading" and "after loading" sample without artificial irradiation.

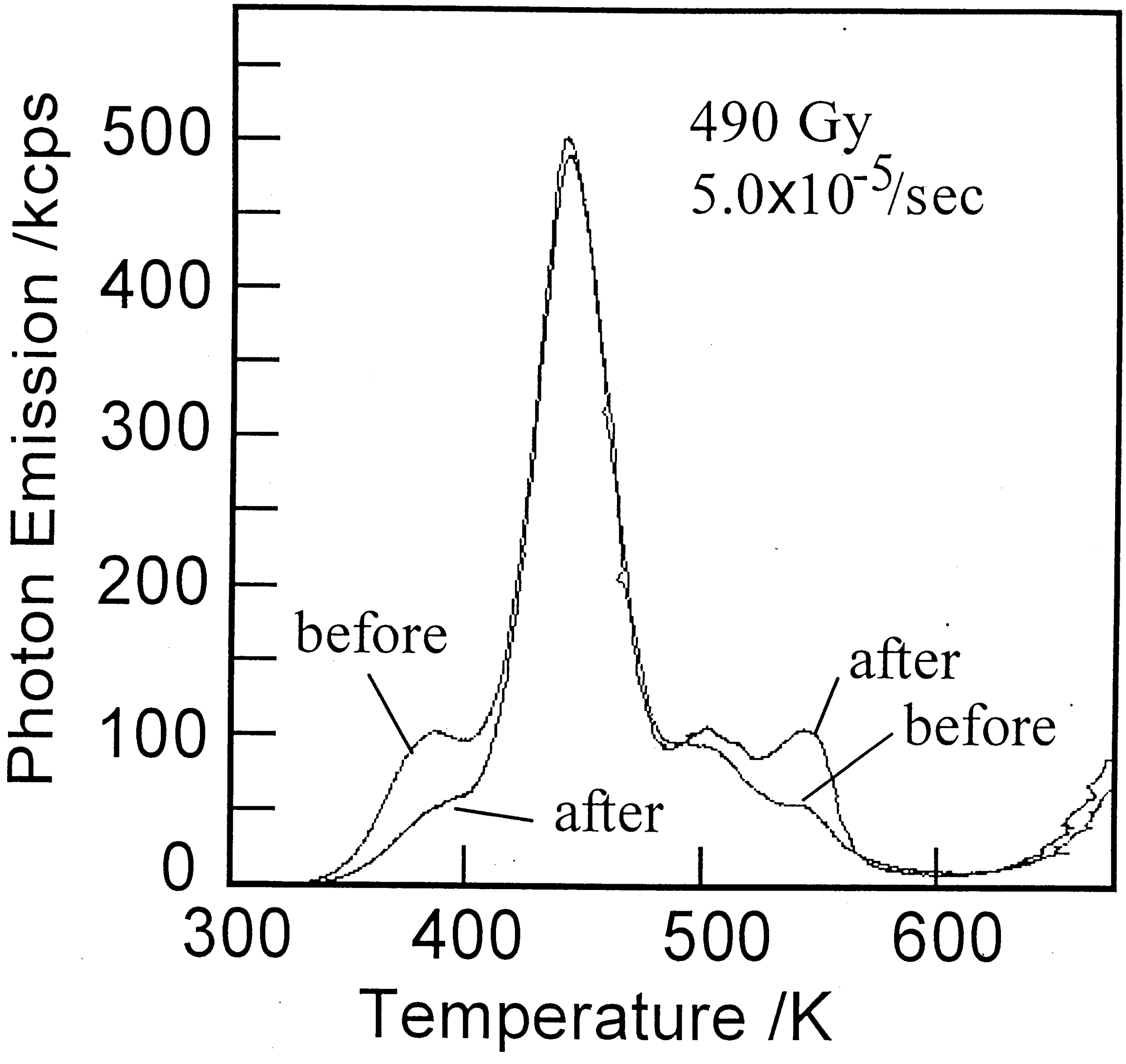

Figure 8. TSL spectra of "before loading" and "after loading" sample. The sample suffered 490 Gy gamma irradiation and was loaded in a strain rate of $5.0\times10^{-5} sec^{-1}$.

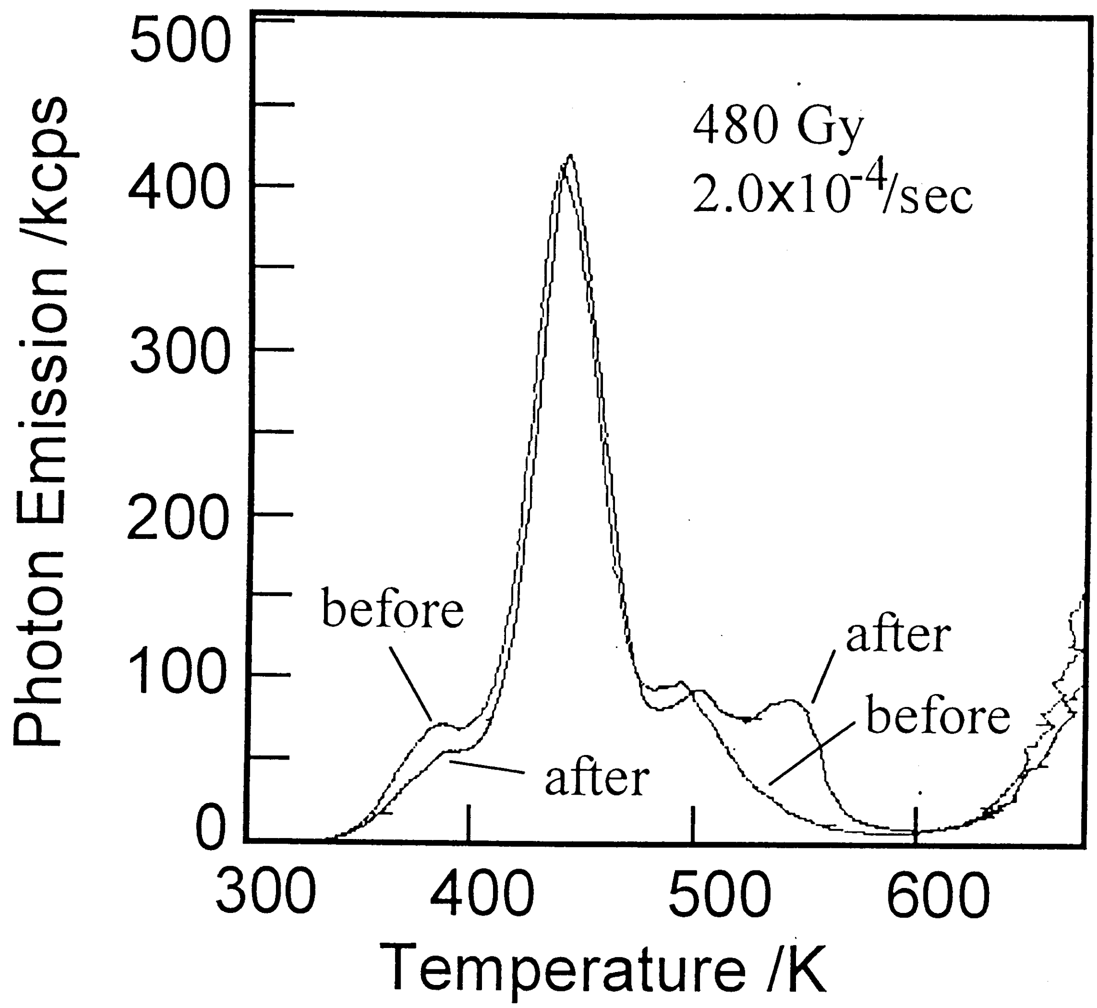

Figure 9. TSL spectra of "before loading" and "after loading" sample with irradiation. The sample suffered 480 Gy gamma dose and was loaded in a strain rate of $2.0 \times 10^{-4} sec^{-1}$.

to the amount of electrons or holes that had been trapped at each site. The TSL signal was discomposed into three peaks and each peak was integrated against temperature as follows: We assume that the TSL signal $I(T)$ consists of three peaks, $I_1(T)$, $I_2(T)$ and $I_3(T)$;

$$I(T) = I_1(T) + I_2(T) + I_3(T), \tag{1}$$

where T is temperature, I_1 has a peak at 390K, I_2 at 440K and I_3 at 540K. We take the TSL signal of non irradiated and "before" loading sample (the signal of 0Gy sample of Figure 3) as reference signal because it appears to consist of only $I_2(T)$, i.e.,

$$I^{ref}(T) = I_2^{ref}(T). \tag{2}$$

$I_2(T)$ of concerning TSL signal is fit as $I_2^{ref}(T)$ multiplied by a constant with least square method and the residual of the fitting represents $I_1(T)$ and $I_3(T)$. Each signal has a range in temperature that $I_i(T)$ is non zero;

$$\begin{aligned} I_i(T) \neq 0 & \qquad T_i^l < T < T_i^u \\ = 0 & \qquad T < T_i^l, T_i^u < T \qquad (i = 1, 2, 3) \end{aligned}$$

Integrated signal intensity S_i is sum of I_i for $T = T_i^l$ to T_i^u;

$$S_i = \int_{T_i^l}^{T_i^u} I_i(T')dT'. \tag{3}$$

Total integrated signal intensity S is

$$S = \int_{T_1^l}^{T_3^u} I(T')dT' = S_1 + S_2 + S_3. \tag{4}$$

We consider integral function of $\tilde{I}(T)$ as

$$\begin{aligned} \tilde{I}(T) &= \int_0^T I(T')dT' \\ &= \int_{T_1^l}^{T} I_1(T')dT' + \int_{T_2^l}^{T} I_2(T')dT' + \int_{T_3^l}^{T} I_3(T')dT'. \end{aligned} \tag{5}$$

In the temperature range above the upper temperature of the peak 1 and below the lower of the peak 3, $\tilde{I}(T)$ is represented as

$$\tilde{I}(T) = S_1 + \tilde{I}_2(T') \qquad (T_1^u < T < T_3^l). \tag{6}$$

This is assumed as

$$\tilde{I}(T) = C_0 + C_1 \tilde{I}^{ref}(T), \tag{7}$$

where C_0 and C_1 are constants that are obtained with least square method. I take the range from 410K to 450K for the least square fitting. Then, S_i will be obtained as

$$\begin{aligned} S_1 &= C_0, \\ S_2 &= C_1 \int_{T_2^l}^{T_2^u} I_2^{ref}(T')dT' = C_1 S^{ref}, \\ S_3 &= S - (S_1 + S_2). \end{aligned} \tag{8}$$

I carried out three TSL measurements for one sample. The numerical values listed in Table 1 are the averages and standard errors for the three measurements. For every "after loading" sample, the decrease of the peak at 390K amounts 30% of that for "before loading" sample and that at 540K gets two to four times of the "before loading." The peak at 440K unchanged in the range of error, though it appears to have slightly increased. It can be interpreted that a part of electrons or holes trapped at relatively unstable site, which shows TSL peak at 390K , was liberated at loading. The liberation of electrons or holes trapped at the site of 390K TSL peak would result in recombination of electrons and holes and the photon emission at loading. This is the SSL model for the photon emission observed at loading experiments. This model is consistent with the observation that non irradiated sample shows no photon emission; There are no peaks at 390K in TSL spectrum of the sample without gamma irradiation. The peaks at higher temperature are stable at loading. This is clearly shown in Figure 5 and 7, where no

Table 1. Integrated TSL signal intensity for each peak

Strain rate /sec^{-1}	Gamma dose /Gy	Integrated peak intensity /10^7counts 390K	440K	540K
5.0×10^{-5}	490			
Before loading		0.94±0.10	4.62±0.37	0.58±0.05
After loading		0.65±0.10	4.97±0.30	1.29±0.20
1.0×10^{-4}	490			
Before loading		0.94±0.10	4.62±0.37	0.58±0.05
After loading		0.66±0.07	4.88±0.26	0.96±0.02
2.0×10^{-4}	480			
Before loading		0.75±0.04	4.23±0.08	0.26±0.18
After loading		0.52±0.02	4.31±0.31	1.11±0.17
2.0×10^{-4}	0			
Before loading		0	1.54±0.08	1.81± 0.23
After loading		0	1.40±0.03	2.41±0.17

photon emission occurs at loading non irradiated sample and the TSL peak at 440K was left unchanged.

The TSL peak at 540K grew at the loading for both irradiated and non irradiated samples. As mentioned previously, the static loading is responsible for the growth of this peak.

4. Conclusions and Discussions

The conclusions of this paper are summarized as follows;

1) I detected luminescence at loading irradiated marble. Non irradiated sample shows no luminescence so that we can say that the phenomenon is SSL.

2) The photon emission intensity increases as strain rate increases. This confirms that the photon emission is directly due to the loading.

3) TSL spectrum change shows that electrons or holes trapped by unstable trap are liberated at loading. The trap with TSL peak temperature of 390K is unstable for loading and ones of higher temperature are stable. SSL can be caused by the recombination of electrons and holes liberated from the unstable site.

4) I found that the loading and fracturing results in the growth of TSL peak at 540K. This phenomenon implies that the deformation progresses with some microscopic processes in which new trapping sites are created and electrons or holes are transferred.

There appeared some problems in this study. One concerns with microscopic mechanism to supply the energy to trapped electrons and holes at loading. In TSL, it is thermal energy, i.e., lattice vibration transfers the energy, and electromagnetic interaction of electrons and holes with photon for OSL. If SSL occurs in the region of elastic deformation, distorted crystal field may supply the energy to the trapped electrons and holes. The trapping site is a local minimum of potential field depending on local disturbance of ion distribution. When the lattice is strained, crystal field distortion can make the minimum of the potential shallow and trapped electrons or holes will be liberated by thermal excitation. There is a possibility of local plastic deformation near the crack tip. If this is the case, moving dislocations interact with point defects and liberate trapped electrons and holes, which is well-known mechanism for deformation luminescence in alkali halides[10)−13)].

The sample with no gamma irradiation does not show luminescence at loading. This suggests that, as for marble, luminescence may not occur in natural state. There are no TSL peaks at 390K for the sample without artificial irradiation and this is the reason photon emission does not occur at loading.

The luminous phenomenon observed in this study is, however, applicable to the prediction of rock bursts in mine. Irradiation with artificial gamma source is possible in mine and one can monitor the risk of fracture in host rock by observing photon emission from the irradiated rock. The sensitivity of the host rock to the stress can be experimentally characterized by the method established in this study. Note that the photon emission precedes the AE activity (see Figure 2). This seems promising for the prediction of rock bursts and saving lives of labors in mine.

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