

Hiroshi Hirose: A Study of Crystalloluminescence

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Crystalloluminescence for three kinds of samples, i. e., $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{K}_3\text{Na}(\text{SO}_4)_2$, and As_2O_3 , was investigated, and the following results were obtained.

- a) Various cracks were found in the crystals that presented crystalloluminescence, and they were very much similar to those of crystals with triboluminescence.
- b) Duration of luminescence of either crystalloluminescence or triboluminescence was less than 10^{-6} sec.
- c) For these three samples the frequencies of luminescence, sounding accompanied with it, and the coincident occurrence of the two were measured and compared with each other. It was confirmed that luminescence and sounding were not independent of each other.
- d) The spectrum of crystalloluminescence for As_2O_3 was found to spread from 620 $\text{m}\mu$ to violet, and its intensity maxima lay near 475 $\text{m}\mu$ and 610 $\text{m}\mu$.

Using transient techniques, the free induction decay time T^*_2 for Cl^{35} was measured for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, KClO_3 , and NaClO_3 . The modes of strain in samples were inferred from changes of T^*_2 with lapse of time.

From the results described above, it appears reasonable to conclude that crystalloluminescence is luminescence which appears when the large strain, made in the course of recrystallization at an appropriate rate, is removed, with the crystals destroyed, by the heat emanated concurrently with the recrystallization.

§ 1. Introduction

It has been known for a long time that as for arsenious anhydride, barium chlorate, alkali halides, and other several substances the luminescence phenomena are observed when their crystals precipitate from the solution. Many findings, such as Trautz and others', were reported in the beginning of this century.¹⁾ But investigation was limited only to the visual observation because the intensity of light was too small and the experimental technique at that time was incomplete, and so the mechanism of the luminescence was not discussed fully.

Since then, Weiser²⁾ studied the ranges of wavelength and intensity distributions of crystalloluminescence and triboluminescence for alkali halide, arsenious anhydride, and double salt of potassium sulfate and sodium sulfate, by means of a set of color filters and photographic plates, and showed there was no difference between them. However, it seems that the precision of his measurements was far from being decisive. Furthermore, though many investigations, Longchambon's³⁾, Racz's⁴⁾ for alkali halide, Tsuda, Takeda and Shibata's⁵⁾ for arsenious anhydride, have been worked out, any conclusive result about luminescence mechanism has not yet been attained.

In this paper, the results of the present experiments, i. e.,

(a) a comparison of crystalloluminescence with triboluminescence, especially an observation of cracks found in the crystals,

(b) a measurement of the duration of crystalloluminescence and triboluminescence, and

(c) a measurement of the relation between crystalloluminescence and sounding accompanying it,

will be described. Samples used were barium chlorate, arsenious anhydride and double salt of potassium sulfate and sodium sulfate.

Moreover, a spectrograph and a measurement of its intensity distribution of arsenious anhydride's crystalloluminescence will be reported. These results have been newly achieved by the author successfully.

The experimental results by means of a transient technique in the pure quadrupole resonance concerning the degree of strain in the crystals presenting crystalloluminescence phenomena will also be presented.

Lastly, a consideration derived from these results will be given.

§ 2. Samples

As the study of crystalloluminescence requires careful attention, samples of "chemical pure" were used in this experiment, and special attention was paid to washing and cleaning-up of the apparatus used. Luminescence was observed in the course of recrystallization from the aqueous solutions of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ and also from HCl solution of As_2O_3 . But as the frequency and the intensity of luminescence were strongly affected by the rate of recrystallization, the concentration of either solution or acid was adjusted so as to meet the optimum condition for luminescence by changing the volume of solution, ambient temperature and so on.

As to the component of double salt of K_2SO_4 and Na_2SO_4 careful attention was required. The mol ratios of the components in the crystals which were purified by recrystallization were:

$$\begin{array}{l} \text{Na}_2\text{SO}_4 \quad : \quad \text{K}_2\text{SO}_4 \\ =1.00 \quad : \quad (3.18 \pm 0.14), \end{array}$$

according to the quantitative analysis of SO_4^{--*} ,

$$\text{and } \begin{array}{l} \text{Na}_2\text{SO}_4 \quad : \quad \text{K}_2\text{SO}_4 \\ =1.00 \quad : \quad (3.00 \pm 0.01), \end{array}$$

according to the quantitative analysis of Na^{+**} .

Bandrowski²⁾ said that crystalloluminescence was most conspicuous when precipitated salt had the definite composition $2 \text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$. Rose^{1,6)} reported that he obtained

* based on the quantitative analysis of SO_4^{--} with barium chloride.

** based on the quantitative analysis on Na^+ with uranyl zinc acetate. This analysis was by courtesy of Mr. T. Atō, Ex-professor of Gifu University.

crystals of $3 \text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ and found crystalloluminescence when he fused two salts of K_2SO_4 and Na_2SO_4 at the ratio of equal mol, dissolving its cool lump into hot water, and made it cool. The crystal had an appearance of a hexagonal prism, was identical with glaserite and will be represented by $\text{K}_3\text{Na}(\text{SO}_4)_2$ in the following.

§ 3. Experiment 1

Experiment (A): 60g of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ was dissolved perfectly into 100cc of water in a glass vessel by heating, and then the solution was cooled naturally down to room temperature. Vigorous luminescence accompanying clear sound was observed in the course of recrystallization. Crystals obtained were of various sizes, some of the largest (larger than 5mm^3) were selected and dried in the vacuum. These crystals will be called Crystal (a) in the following. They were monoclinic (gypsum type) and some of them had cracks which were parallel to the (110) or $(\bar{1}10)$ cleavage plane.

Experiment (B) : On a heater was placed an asbestos plate with enough thickness, upon which a nickel-plated copper plate was piled, its temperature being measured by a thermocouple. When Crystal (a) was dropped upon the copper plate of about 100°C , luminescence was observed clearly. Picking up the dropped crystals rapidly from it, many crystals were found to have various cracks. Planes of cracks were mainly of plane (110) or $(\bar{1}10)$. These will be called Crystal (b) in the following.

Experiment (C) : No luminescence was observed though the same operation was repeated over again on Crystal(b) as in Experiment(B). The crystal which has undergone this operation will be called Crystal (c) in the following.

Experiment (D) : After Crystal (a) was heated gradually in the air, annealed for an hour at about 100°C , and cooled gradually to room temperature, no luminescence was observed under the same operation as in Experiment (B). The crystal annealed in this way will be called Crystal (d) in the following.

Experiment(E) : When either of Crystal (a), (b), (c) or (d) was dropped upon the copper plate of about 150°C , it splitted, emitted weak greenish light with sounding, and at last turned into white powder deprived of water of crystallization. Luminescence was emitted in so far as the crystal held a crystalline structure containing water of crystallization.

Experiment (F) : All crystals of (a), (b), (c) and (d) emitted weak light when they were broken mechanically. For example, they emitted light even when they were crashed by means of two sheets of glass plate.

Similar experiments were worked out also for $\text{K}_3\text{Na}(\text{SO}_4)_2$ and As_2O_3 . However, they differed from Experiment (A) where 17.6 g of K_2SO_4 together with 14.4 g of Na_2SO_4 , and 6 g of As_2O_3 were dissolved, by heating, in 100cc of water and in 50cc of 4 N HCl, respectively. Cracks produced in $\text{K}_3\text{Na}(\text{SO}_4)_2$ crystals (hexagonal prisms) were especially clear, and these cracks were found in all the crystals which seemed to have presen-

ted crystalloluminescence. Most of them were parallel to the plane (0001). Most of the cracks observed in As_2O_3 crystals (octahedron cubic) were parallel to (111) plane.

Results described so far are summarized in Table I, where "S", "L" or "C" represent the case where either of sounding, emission of light or crack was found respectively; "X", the case of of no emission; and * indicates that the phenomenon in question was found newly in the present experiment.

Table I.

Experiment		Sample	$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{Na}(\text{SO}_4)_2$	As_2O_3
(A) in case of recrystallization from solution.			L, S*, C*	L, S, C,	L, S, C
in case of dropping crystals on 100°C hot plate.	(B) Crystal (a)		L*, S*, C*	L, S, C	L*, S*, C*
	(C) Crystal (b)		X	X	X
	(D) Crystal (d)		X	X	X
(E) in case of dropping crystals on 150°C hot plate.	Crystal (a), (b), (c), (d)		L*, S*, C*	L, S, C	L*, S*, C*
(F) in case of mechanical breaking.	Crystal (a), (b), (c), (d)		L	L	L

§ 4. Experiment 2

Experiments were performed on the measurement of duration of crystalloluminescence, the measurement of the relation between luminescence and sound accompanying it, and photographing of spectrum of crystalloluminescence. They will be described section by section.

§ 4.1. Measurement of Duration of Luminescence

In all the cases, which were marked by "L" in Table I, light was detected by a photomultiplier tube (RCA 931A). Its photoelectric currents were amplified with a pre-and a main amplifier. And duration of luminescence was measured through a synchroscope (National CT-511A).

Apparatus. The pre-amplifier was a broad-band amplifier which involved three tubes 6AK5 and one tube 12BY7A, and its output was connected with a coaxial cable of 300 ohms. The main amplifier was composed of three parts: (1) a push-pull amplifier involving two tubes 12BY7A, (2) a circuit which involved one tube 12BY7A and two crystal diodes OA-81, and generated a brilliance modulation voltage and a horizontal sweep voltage applied into the synchroscope, and (3) a time checking vibrator involving one tube 12BY7A. These two amplifiers were activated by d. c. power from batteries in

order to keep the noise level as low as possible. The gain of circuits involving pre-and main amplifiers and a synchroscope was 59.5 db for 100 Kc/sec., 56.5 db for 500 c/sec. and 1.7 Mc/sec., and nearly constant from 500 c/sec. to 1.7 Mc/sec.

Procedures. In order to examine time characteristics of these apparatuses an experiment shown in Fig. 1 was performed. Light emitted from a tungsten lamp S lit by d. c. source was converged into slit S₁ through lens L₁. The light emitted from S₁ was conver-

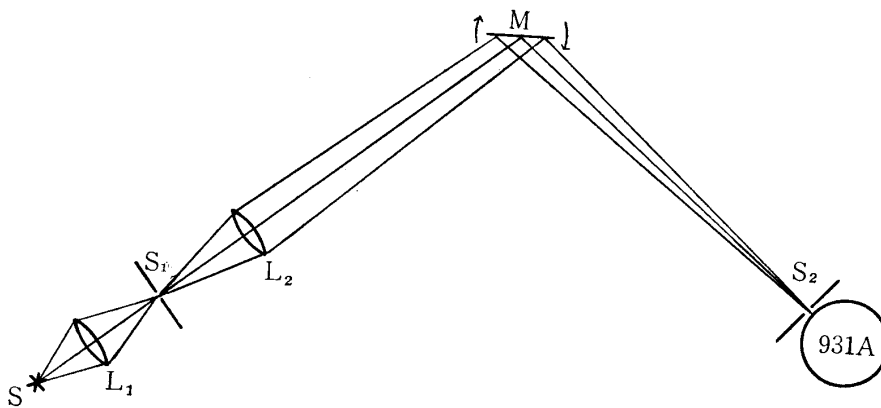


Fig. 1. Schematic diagram of the apparatus to examine time characteristics.
 S: Light source, S₁, S₂: Slit, L₁, L₂: Lens, M: Rotating plane mirror.

ged into slit S₂ through lens L₂ and rotating plane mirror M to make the image of S₁.

If the rotational frequency of the plane mirror is $n \text{ sec}^{-1}$, the distance of M from S₂ is D cm, width of image of S₁ made at S₂ is a₁cm, and width of S₂ is a₂cm, then the time interval Δt during which the photomultiplier tube is illuminated is expressed by the following equation:

$$\Delta t = \frac{a_1 + a_2}{4\pi n D} \text{ (sec.)} \dots\dots\dots(1)$$

Photocurrent by this light produced an oscillogram as shown in Fig. 2a, Plate I.

Similarly an oscillogram of an a. c. voltage generated by the time checking vibrator involved in the main amplifier was obtained (Fig. 2b, Plate I.) This frequency was measured by a dipmeter and moreover was compared with the result measured by a broadband vibrator (Tōa Denpa-CR 10KB). As the frequency could be measured by these methods, the time of horizontal sweep could be obtained. Thus the time interval of illuminating the photomultiplier was estimated and was found to agree with the value calculated by Eq. (1). Therefore the time characteristics of the amplifiers may be regarded as satisfactory for the purpose of measuring the duration of luminescence.

Results and considerations. In this experiment values of a₁, a₂ and D were 0.18 cm,

0.18cm and 233 cm respectively. The plane mirror was light and small, and was attached directly to a shaft of a synchronous motor whose rotational frequency n was 30 sec^{-1} . Putting these values into Eq. (1), $\Delta t = 4.2 \times 10^{-6} \text{ sec.}$ was obtained. A photograph under such a condition is shown in Fig. 2a, Plate I. A photograph taken in the case of vibration with a frequency of 1.22 Mc/sec., which was produced by the checking vibrator, is Fig. 2b, Plate I. Error of this frequency value was less than 5 percent. In Fig. 2c, Plate I, photoelectric current of crystalloluminescence of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ is shown. These three photographs were taken by overlapping some tens of the repeated images on the cathode-ray tube, because a single image was too faint to be taken by photograph. The large width of the image in Fig. 2a seemed to be mainly due to the vibration of the mirror. The same defect in Fig. 2c also seemed to come from the irregular deviation of the image caused by the irregularity of luminescence intensity. Since the time duration for one wave in the picture was $8.2 \times 10^{-7} \text{ sec.}$ in Fig. 2b, time of illumination in Fig. 2a corresponded to about $4 \times 10^{-6} \text{ sec.}$, which agreed well with $4.2 \times 10^{-6} \text{ sec.}$ obtained by calculation. Thus it turned out from Fig. 2c that the duration of crystalloluminescence of barium chlorate seemed to be less than 10^{-6} sec. The duration of crystalloluminescence of either $\text{K}_3\text{Na}(\text{SO}_4)_2$ or As_2O_3 was found, by the similar procedure as the above, to be less than 10^{-6} sec. Durations of light in Experiments (B), (E) and (F) (these luminescences were due to triboluminescence as explained later), were estimated, but any difference between them could not be found.

Stranski, Strauss and Wolff⁷⁾ measured the duration of triboluminescence for single crystals of arsenolite and claudetite by using a photomultiplier tube, (both are natural crystals of As_2O_3), and obtained the value 10^{-4} sec. or less. This value is remarkably larger than that of the present experiment ($< 10^{-6} \text{ sec.}$). This discrepancy may be due to the fact that they took several luminescences emitted in succession.

§ 4.2. Relations between Frequencies of Luminescence and of Sounding

As the fact that crystalloluminescence accompanied sounding was confirmed in Experiment 1, relations between frequencies of luminescence and sounding were worked out. Since the cooling rate of a solution is a kind of index for progressive states of recrystallization, relations between the temperature of a solution and the frequencies of luminescence and sounding were also examined.

Apparatus. Luminescence was received by a photomultiplier tube and sound by a crystal microphone (Crown Co.). Frequencies of both luminescence and sounding were measured through counting circuits shown in a block diagram of Fig. 3. This circuit was divided into two parts: a system for light and a system for sound. The system for light was composed of a pre-amplifier (LI), a main amplifier (LII), a discriminator (LIII), a counter (Light) and a delay circuit (LIV); the system for sound was composed of a pre-amplifier (SI), a selector (SII), a discriminator (SIII) and a counter (Sound).

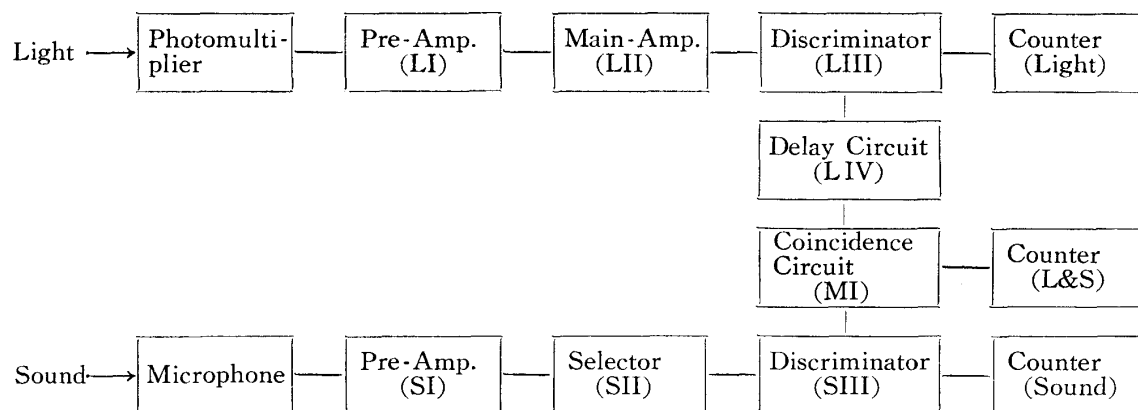


Fig. 3. Block diagram of the apparatus for Experiment 2.

The coincidence circuit (M I) and the counter (L & S) were added to study the coincidency of luminescence and sounding.

L I and L II were the same as those used in the experiments in § 4.1. L III was the discriminator in which trigger level could be selected at will using a tube 12 AU7, and in actual measurement this level was set at 5.0 volts. Voltage of output pulses was kept constant at 30 volts. These output pulses were led to the counter (Light) and L IV was a delay circuit involving a tube 6SN7, and was adjusted so that trigger level could be selected freely as in L III, the level of which was kept at 7.0 volts in measuring. The output pulses had duration of 0.6m sec. These pulses were led to MI.

S I was a pre-amplifier involving two tubes of 6SJ7 and one 12 AU7, output pulse of this was led to S II. S II was a selector involving each one of the tubes 6 SJ 7, 6 AC 7, 6SN7 and crystal diode OA-81, and could amplify pulses of frequency range from 800 c/sec. to 50,000 c/sec. The band, in which S/N of circuit of sound system used was maximum, was selected in the measurement and was shown in Fig.4.

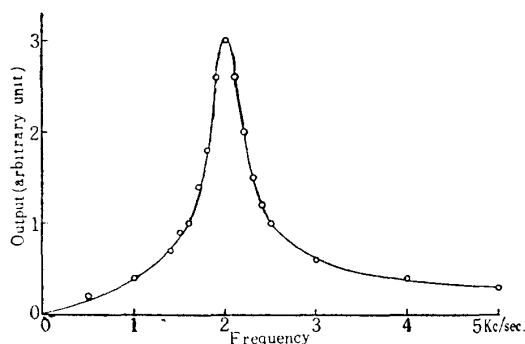


Fig. 4. Characteristic curve of the selector (S II) at actual measuring.

The gain of the pre-amplifier and the selector was 99 db for 2 Kc/sec. S III was the

discriminator involving each one of 6SJ7 and 6SN7, its trigger level was 1.0 volt and the recovery time was 0.5m sec. Its output pulse was led to the counter (Sound) and a coincidence circuit (MI). MI involved 6BN7, and produced a pulse which lasted only during the time interval of overlapping of light- and sound-pulses. Its output pulse was led to the counter (L & S). All counters were of SA-1000 type (Kōbe Kōgyō), and their resolution was 2μ sec. For every circuit described above, except counters, batteries with a large capacity were used as a source to keep the noise level as low as possible.

The microphone used for the measurement was constructed by connecting Rochelle salt and the bottom of the flask with a metal bar (what was called a connecting pin), after taking off the protective cover and vibration plate from a usual crystal microphone. The temperature of solution was measured as accurately as $1/20^\circ\text{C}$ by a bridge-connected thermister (Tōshiba C-13) and recorded by a tapping-recording ampere meter (Yokogawa 100 microamperes) with the lapse of time.

Procedures. Samples were dissolved in round bottomed flasks with a capacity of 50 cc. Then they were placed to be cooled down naturally in the dark room isolated from outside. The frequencies of luminescence and sounding, which were produced by these samples while they cooled down, and the temperatures of solutions were recorded as functions of time lapse. Noise count could be kept less than one per 10 minutes, since batteries were used as a power source, the trigger level was adjusted high, and the experiments were performed only when the surroundings were quiet.

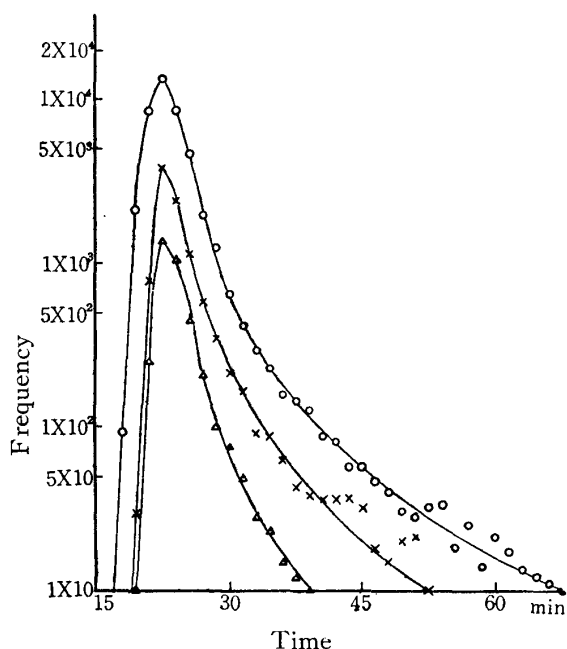


Fig. 5a. Time changes of frequencies of crystalloluminescence(\times), sounding (\circ), and coincident occurrence of both (Δ) per 90 seconds.
Sample: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.

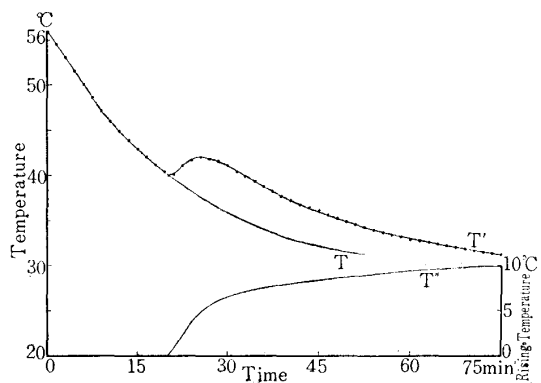


Fig. 5b. Time changes of temperature of solution. T' : Curve of measured temperature, T : Cooling curve without recrystallization, T'' : Amount of temperature rising owing to recrystallization under the assumption of no cooling (according to Eq. (5)). The vertical scale in this case is represented on the right side of this figure.
Sample: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.

If the duration of a pulse in the system for light were too short, the coincident occurrence of light and sound would be missed. The reason is this: the electric signal of sound is somewhat delayed comparing with that of light, though they are produced at the same instant from the sample⁸⁾. Therefore, the duration of a pulse in the system for light was prolonged as long as 0.6m sec.

Results. Typical results of measurement will be explained in the following. Frequencies of luminescence, sounding and coincident occurrence of both were recorded per 90sec., in the case where 16g of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ was dissolved in 23cc of water and cooled down naturally. This result is shown in Fig. 5a. Temperature change of solution in this example is shown by curve T' in Figs. 5b and c. The ambient temperature was 27.40°C . Similarly, the results on measurement of cooling rate, in the case where 3.97g of K_2SO_4 and 3.22g of Na_2SO_4 were dissolved in 21.1cc of water, are shown by curve T' in Figs. 6b and c. The ambient temperature was 26.40°C . The results on measurement of cooling rate, in the case where 1.9g of As_2O_3 was dissolved in 20cc of 4.4N HCl, are shown by curve T' in Figs. 7b and c. The ambient temperature was 25.50°C .

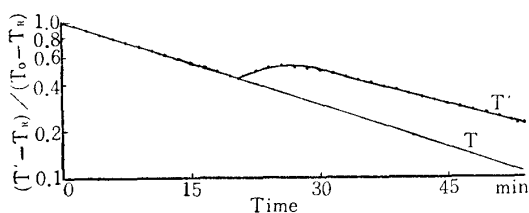


Fig. 5c. Time changes of temperature of solution. T and T' represent the cooling curve without recrystallization and the curve of measured temperature respectively, and T_R , T_0 , and T' in the vertical axis represent room temperature, temperature of solution at the beginning of measurement and measured temperature of solution respectively. Sample: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.

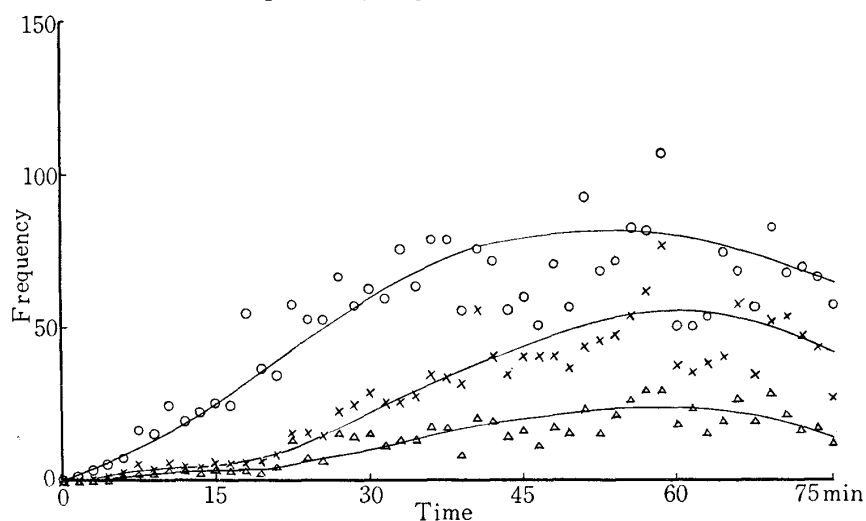


Fig. 6a. Same as Fig. 5a. Sample: $\text{K}_3\text{Na}(\text{SO}_4)_2$.

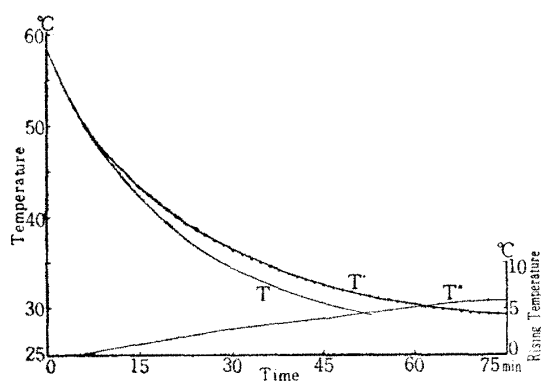


Fig. 6b. Same as Fig. 5b.
Sample: $K_3Na(SO_4)_2$.

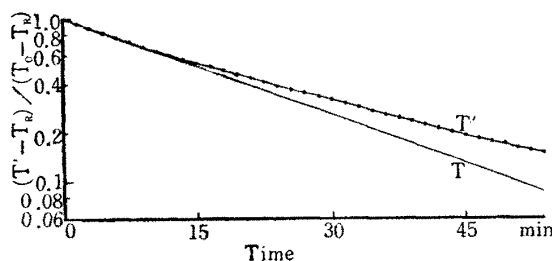


Fig. 6c. Same as Fig. 5c.
Sample: $K_3Na(SO_4)_2$.

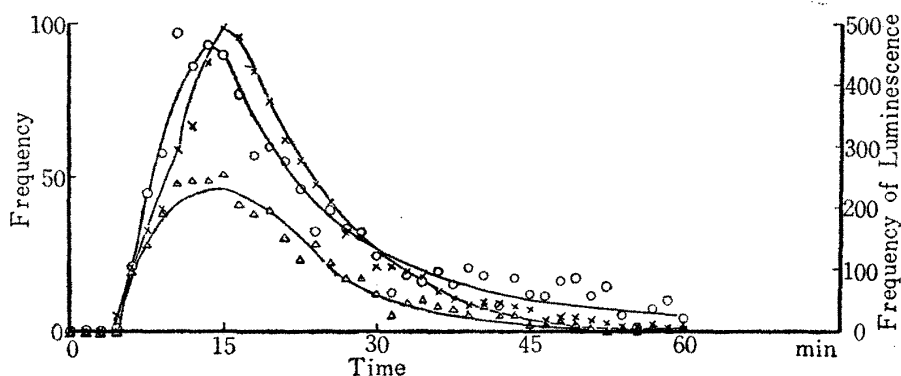


Fig. 7a. Same as Fig. 5a.
Sample: As_2O_3 .

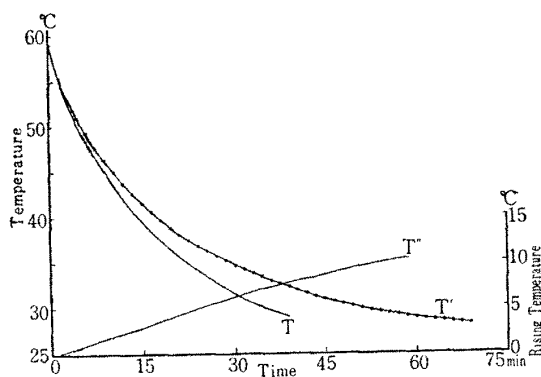


Fig. 7b. Same as Fig. 5b.
Sample: As_2O_3 .

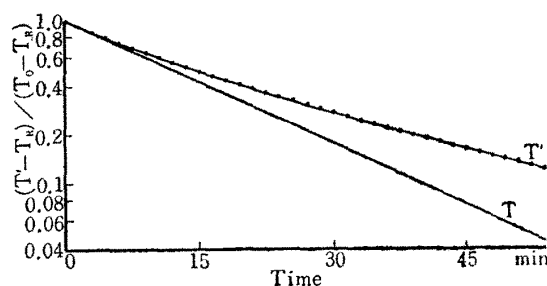


Fig. 7c. Same as Fig. 5c.
Sample: As_2O_3 .

Considerations on relations between luminescence and sounding will be discussed later in § 6, taking these results as bases.

§ 4.3. Spectrum of Crystalloluminescence of As_2O_3

As the intensity of crystalloluminescence is very small, it is quite difficult to take spectrograms of the luminescence. Nevertheless, a successful spectrogram of crystalloluminescence was obtained in this experiment by using As_2O_3 as a sample.

Apparatus. The spectrograph used in the present experiment was constructed by the author and his coworkers⁹⁾; either of its collimeter lens and camera lens had an aperture ratio of F/1, a focal length of 10cm (Kyōto, Matoba); its prism had an angle of 60°, 10 cm in height, 12.5 cm in side, and the material was F 1 glass. Fuji SSS film was used for photographing.

Procedures. 50cc of 4.4 N HCl and 6g of As_2O_3 were heated in a round bottomed flask of capacity 100cc with an air condenser. After As_2O_3 was completely dissolved, it was cooled down naturally. It began to emit light as a considerable amount of As_2O_3 octahedron cubic was seen recrystallized on the wall of the flask and on the surface of solution. When the flask was shaken softly at this instant, it emitted light so vigorously for about 10 sec. that the whole flask seemed bright. This light was led to the slit of the spectrograph.

Such an operation was repeated one hundred times. Consequently a spectrogram was taken with the net exposure time of about 20min. Experiments were performed so carefully that the dark room might be kept perfect to take spectrogram as the light was very weak.

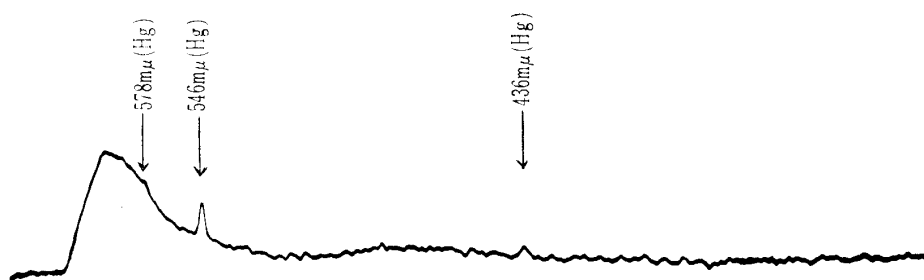


Fig. 8a. The microphotometer curve of spectrum of crystalloluminescence. Slit width: 0.15mm, Exposure: 20min., Sample: As_2O_3 ,

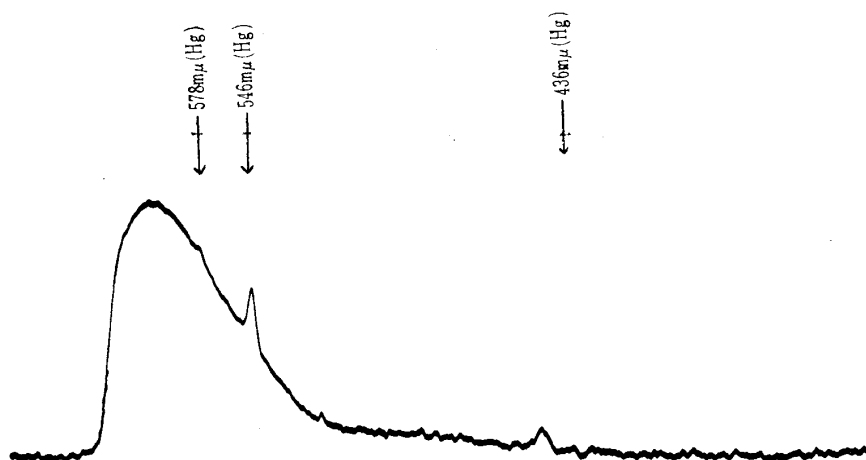


Fig. 8b. The microphotometer curve of comparison spectrum of 100-watt tungsten lamp. Slit width: 0.01mm, Exposure: 0.5 sec.

Results. Fig. 8a shows a microphotometer curve of the spectrogram obtained when the width of slit of spectrograph was 0.15mm. Mercury spectrum was used as a standard of wavelengths. In order to examine the characteristics of the photographic film, a spectrogram was taken, using 100-watt tungsten lamp as a light source, with 0.01mm of slit width and 0.5 sec. of exposure time. This microphotometer curve is shown in Fig. 8b. Comparing these two curves, the following conclusions on the distribution of intensity were formulated.

(1) In the region of wavelengths shorter than $500\text{ m}\mu$, the maximum intensity lay near $475\text{ m}\mu$, wherefrom the intensity on either side of long and short wavelengths was distributed decreasingly.

(2) In the region of wavelengths longer than $500\text{ m}\mu$, the subsidiary intensity maximum lay near $610\text{ m}\mu$, and the edge at long wavelength side was $620\text{ m}\mu$.

(3) The intensity in the region of wavelengths shorter than $500\text{ m}\mu$ was larger than that in the region of wavelengths longer than $500\text{ m}\mu$.

Weiser²⁾, who studied by a set of color filters and photoplates, reported that in the crystalloluminescence of As_2O_3 a small amount of green light existed and light from greenish blue to violet was as rich as in the white light, while, on the contrary, light from red to yellow did not exist. However, in the present experiment, though red light could not be observed, lights in all region from yellow to violet were recognized. Namely, Weiser missed yellow light. Stranski and his coworkers⁷⁾ reported the spectrum of triboluminescence of arsenolite spread from 3000 \AA or less to red, but red light was not found in the present experiment on As_2O_3 crystalloluminescence.

§ 5. Experiment 3

Since it should be expected that crystals which are capable of emitting either crystalloluminescence or triboluminescence have strains in them, they were examined under a phase contrast microscope and a polarizing microscope. But no strains were detected. Therefore, using transient techniques, the free induction decay time T^*_2 for Cl^{35} in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ was measured and the existence of strains in samples was inferred from the changes of T^*_2 with lapse of time.

Pure quadrupole resonance experiments on nuclei have been performed by many scientists and their reports have come up to a great amount.^{10,11)} Thus it was indicated that Gaussian free induction decay curve was affected mainly by (1) the magnetic dipole-dipole interaction with neighboring nuclei and (2) the distribution of electric field gradients in the crystal due to strain, imperfection and temperature gradient.^{12,13)} However, the measured value of free induction decay time T^*_2 according to mechanism (1) is considerably larger, and so in order to obtain this value the sample must be made carefully enough not to be affected by mechanism (2). Namely, sufficient time must be required for recrystallization of samples. Hence T^*_2 of crystals recrystallized at a considerably rapid rate

may be due mainly to mechanism (2). The value of T^*_2 from mechanism (1) being independent of the lapse of time after recrystallization, if measured values of T^*_2 change with the lapse of time, this change should be assumed to be caused by mechanism (2).

From this point of view pure quadrupole resonance experiments were performed for Cl^{35} in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ which was capable of either crystallo- or tribo-luminescence, KClO_3 which was capable of emitting triboluminescence only, and NaClO_3 which produced neither of luminescence.

§ 5.1. Apparatus and Procedures

The electric circuit used is shown in the block diagram (Fig. 9). It was composed of a pulse generator which generated gate pulses of which duration could be adjusted, a transmitter which could be put on and off by this gate pulse, a superheterodyne receiver

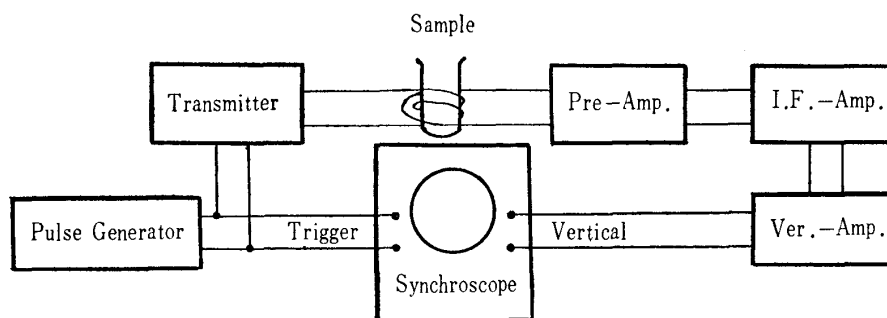


Fig. 9. Block diagram of apparatus for Exp. 3.

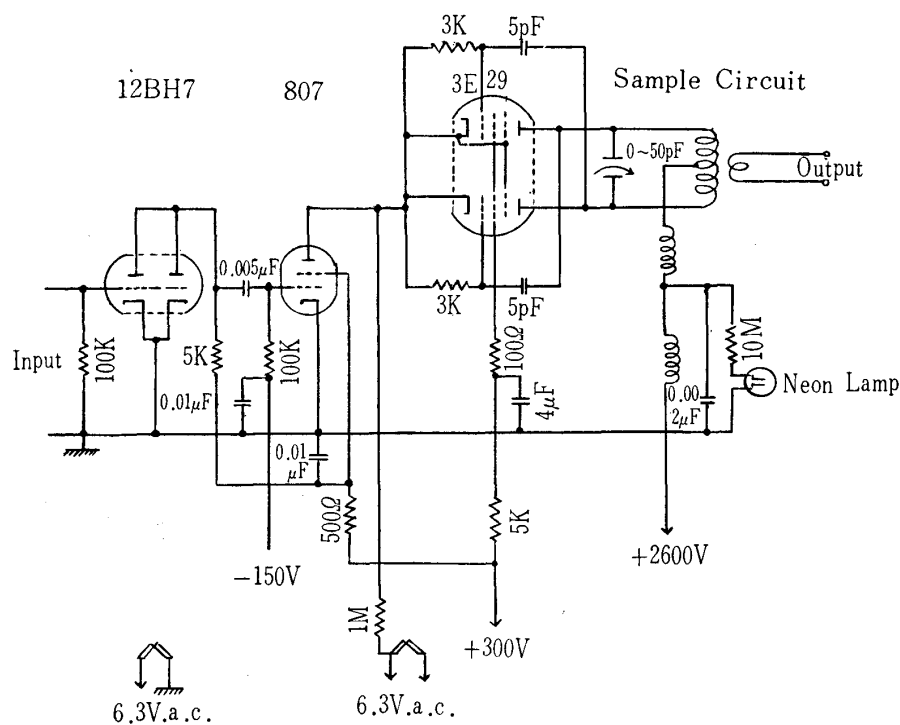


Fig. 10. Transmitter.

with a high frequency amplifier of cascode circuit, which was used for discriminating signals, and a synchroscope which was used for observing signals discriminated by the receiver.

Matters to be attended to the main parts of apparatus and samples will be summarized in the following.

(1) **Transmitter.** Transmitter circuit is shown in Fig. 10. Colpitts type push-pull transmitter circuit involved one pulse modifying tube 3E29, which was operated by a tube 807 only within the duration of gate pulse. The transmitting coil in the sample circuit was a plug-in coil which provided samples with a high frequency magnetic field and was set to operate as a receiving coil immediately after the field was cut off. And it could be tuned continuously between 28Mc/sec. and 35Mc/sec. by a variable condenser placed in the circuit.

In order to make the duration of the high frequency magnetic field provided to the sample equal to that of the gate pulse, "Q" of the coil had to be made as small as possible, but in that case S/N became undesirable when it was used as a receiving coil. Therefore a shunt resistor was not used in this circuit. For this reason the duration of the transmitting pulse which appeared on the synchroscope became a little longer than that of the gate pulse, but its time difference was less than $6\mu\text{sec}$.

(2) **Pre-amplifier and intermediate frequency amplifier.** The pre-amplifier involved a cascode tuner (Star-TU12) and the first stage of the I. F. amplifier. The I. F. amplifier was composed of the second and third stages of the I. F. amplifier, a wave detector with a diode and a audio frequency output circuit by a cathode follower. These were similar to those described in the report of Buchta, Gutowsky and Woessner¹⁴).

In order to get the appropriate level for the diode, the maximum amplification degree of the I. F. amplifier had to be about 10^6 . Every stage of the amplifier was saturated while the strong transmitting pulse was activating and it had to be adjusted to recover itself within $5\mu\text{sec}$., after the pulse ceased. The amplifiers were constructed to satisfy this condition.

In addition, L-C circuits in every stage had to be set so that transient phenomena following the saturation should become lower within $5\mu\text{sec}$. than the noise level that was amplified in the preceding stage. Therefore the amplification stages were arranged in maximally flat staggered triples.

(3) **Samples.** Samples were prepared by the recrystallization from the solutions of "chemical pure" reagents which were commercially available. In general, the rate of recrystallization played an important role in the experiment on crystalloluminescence. As for every sample of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, KClO_3 and NaClO_3 , aqueous solutions of 100°C were placed for about two hours at room temperature to finish recrystallization. Immediately after the crystals were picked up from the solution, they were dried perfectly in the vacuum and sealed into glass tubings.

All the measurements were performed at room temperature (30°C), and especially an observation (photographing) of a free induction decay curve of one sample was done in a few seconds not to cause a temperature gradient in the sample.

§ 5.2. Results

Free induction decay curves for these samples agreed well with Gaussian curve within the experimental error. A typical example is illustrated in Fig. 11, Plate II, which is a curve for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. Each free induction decay time T_2^* evaluated from the curve was compared with T_2^* of the sample which was annealed at 100°C for five hours 30 days after it had been recrystallized. T_2^* for the latter will be expressed by $T_{2\infty}^*$ in the following. The changes of $T_2^*/T_{2\infty}^*$ with lapse of time are shown in Fig. 12, of which the horizontal axis represents the time which elapsed since the sample was recrystallized. The values of $T_{2\infty}^*$ are shown in Table II.

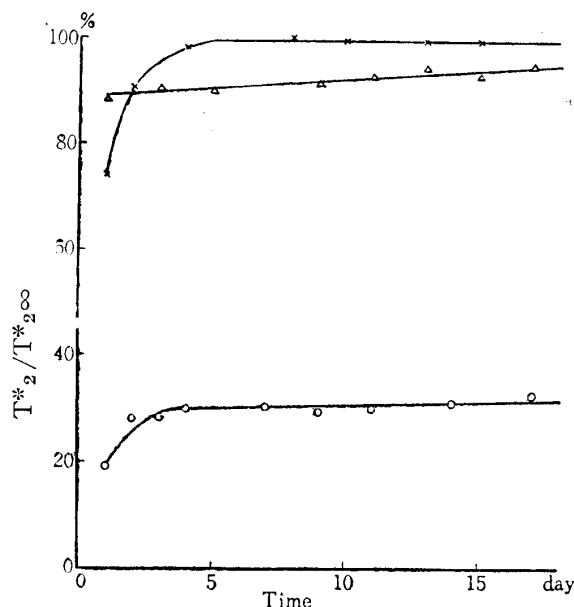


Fig. 12. Time changes of $T_2^*/T_{2\infty}^*$. ○: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, ×: KClO_3 , △: NaClO_3 .

Table II. Measured values of frequency and $T_{2\infty}^*$.

	Frequency(Mc/sec.)	$T_{2\infty}^*$ ($\times 10^{-5}\text{sec.}$)
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	29.4	10.6
KClO_3	28.1	18.7
NaClO_3	29.9	22.7

Since the free induction decay curves agreed well with Gaussian curve, mechanisms responsible for them were considered to be the following three.^{12,15)} (1) the magnetic dipole-dipole interaction with neighboring nuclei, (2) the distribution of electric field

gradients in the crystal which may be caused by a too fast disorderly growth of the crystal, and (3) Zeeman effect caused by the earth's magnetic field. In general, T^*_2 of the crystal produced by the recrystallization method does not take a definite value but shows a fluctuation and the maximum value of T^*_2 is considered to be caused by mechanism (1) and the deviation of value of T^*_2 , by mechanism by mechanism (2).^{12,13)} The effect by mechanism (3) is so small¹¹⁾ that it may be neglected in the present case. Consequently, changes in T^*_2 with lapse of time were considered mainly due to mechanism (2).

As the samples used in this experiment were polycrystals, T^*_2 may be affected by both (1) and (2). Now the relative broadening will be obtained by taking $T^*_{2\infty}$ as a standard. If Γ and Γ_∞ represent the actual line width and the line width corresponding to $T^*_{2\infty}$ respectively, the relative broadening is defined by $(\Gamma - \Gamma_\infty) / \Gamma_\infty$.¹⁶⁾ This relative broadening may be considered as a measure indicating the degree of strains. Changes of this value with lapse of time are shown in Fig. 13. Fig. 13 illustrates clearly that the strains in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ were the largest in amount of the three and decreased rapidly in the beginning and then gradually as the time elapsed. Though less than that in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, strains existed also in KClO_3 and their states of decreasing were similar to the former. But in NaClO_3 strains decreased gradually from the beginning and no rapid changes were found.

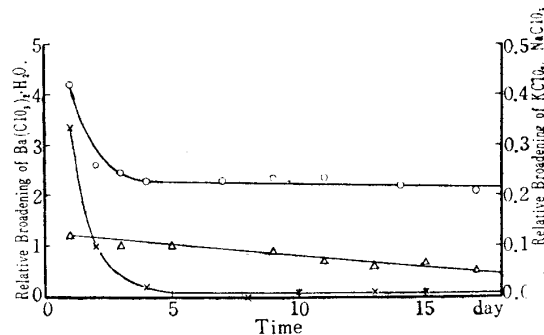


Fig. 13. Time changes of relative broadening.
 ○: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. ×: KClO_3 ,
 △: NaClO_3 .

In the next place, samples recrystallized one whole day before were crushed down into powder with a mortar and, about four hours later, T^*_2 for them were measured. As for crystal $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, T^*_2 was from 2.0×10^{-5} sec. to 3.0×10^{-5} sec.; for KClO_3 , from 13.8×10^{-5} sec. to 14.5×10^{-5} sec.; and for NaClO_3 , scarcely any change was found. This indicates that in newly recrystallized $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and KClO_3 there exist strains which are easily removed just by mechanical pulverization.

§ 6. Considerations on the Results of Experiment

First of all relations between frequencies of luminescence and of sounding will be considered in order to infer the mechanism of crystalloluminescence. For this purpose, a

frequency of coincidental detection of the two sorts of pulses, one by light and the other by sound, each being generated quite at random, will be analysed. Now let the number of pulses by light per second, that by sound per second, the duration of these two pulses, and the frequency of their casually coincident occurrence per 90 seconds be represented by N_L , N_S , T_L ($=0.6 \times 10^{-3}$ sec.), and T_S ($=0.5 \times 10^{-3}$ sec.), and n , respectively. If N_L and N_S are small, the following relations may be valid.

$$n \approx 90 N_L N_S (T_L + T_S)^* \dots \dots \dots (2)$$

N_L and N_S were estimated to be 1/90 of values shown in Figs. 5a, 6a, and 7a. Except the values near the maxima of the curves in Figs. 5a and 7a, n was rather small for all other results of experiments and were less than unity.

When N_L is relatively large and N_S is small as is the case shown in the vicinity of the maximum of the curve in Fig. 7a, the following considerations may be required.

(1) The duration of pulse by light registered by the counter (Light) was less than 10^{-6} sec., but this was prolonged to 0.6×10^{-3} sec. ($=T_L$) in the coincidence observation, as mentioned in regard to the procedures of experiment. Therefore pulses by light generated in the interval of less than 0.6×10^{-3} sec. were missed from counting.

(2) Two pulses by light with duration T_L happen to be generated within less than $(T_L + T_S)$.

In order to consider these two points, Poisson's law¹⁷⁾ of small probability:

$$p(K) = \frac{(\nu T)^K}{K!} e^{-\nu T} \dots \dots \dots (3)$$

was assumed to represent the frequency of the generation of light pulses, where ν stands for the number of pulses per second, T the time interval, K the number of pulses put into T , and $p(K)$ its probability.

In this case, the number of light pulses generated in second may also be considered to be equal to the number counted by the counter (Light). Let this value be N_L . N_L' is theoretical number of light pulses to be counted per second when the consideration (1) holds good, and N_L'' is the corresponding one when T_L is exchanged for $(T_L + T_S)$.

When N_L' and N_L'' were estimated by Eq. (3) for the maximum measured value of As_2O_3 in Fig. 7a, the following was obtained:

$$N_L' \approx N_L'' \approx 5.5 \approx N_L.$$

This has revealed that as to the maximum value and its neighborhood shown in Fig. 7a no consideration was necessary concerning the two points in question mentioned above. Consequently, Eq. (2) gives $n=0.54$ and this value is very small compared with 51 of

* If two sorts of pulses happen to overlap each other the counter (L&S) counts one independent of time interval of overlapping. Consequently, if a pulse of one sort is generated within $(T_L + T_S)$ after the preceding pulse of the other sort, these two are observed to be coincident. If N_L light pulses appear per second, the probability for one sound pulse to be coincidentally observed is $N_L \times (T_L + T_S)$. Therefore, if N_S sound pulses appear per second, the frequency of coincidental observations per second is $N_L N_S (T_L + T_S)$.

the number obtained from the coincidence observation.

Where values of N_L and N_S were extremely large as is the case with the measurement for $Ba(ClO_3)_2 \cdot H_2O$ (Fig. 5a) Eq. (2) was no longer valid. Assuming that only one sound pulse is generated within $(T_L + T_S)$ and Eq. (3) holds good for light pulses, Eq. (2) is transformed into

$$n \approx 90 N_S \{N'_S (T_L + T_S) - \frac{T_S}{2} (N'_L - N_L''')\}^*, \dots\dots\dots(4)$$

where $N_L''' = N_L e^{-NL(T_L+T_S)}$.

The receiver was improved to make the duration of sounding as short as possible. Fig. 14, Plate II shows an oscillogram of the sound wave from $Ba(ClO_3)_2 \cdot H_2O$ obtained through a synchroscope. Its duration was about 0.8 m sec., but sometimes it went over 1 m sec. (For this reason the duration of sound pulse in S III was cut off at 0.5 m sec.) Consequently it can be assumed, without a serious mistake, that more than one sound pulse are not generated within $(T_L + T_S) = 1.1m$ sec. Therefore Eq.(4) can be used, without an extremely large error, to calculate the value near the maximum of measured values for $Ba(ClO_3)_2 \cdot H_2O$. Accordingly estimation by means of Eq.(4) may not be insignificant. Evaluation of n for the maximum measured value for $Ba(ClO_3)_2 \cdot H_2O$ yielded

$n \approx 580$, from $N_L = \frac{3807}{90} = 42.3, N_S = \frac{13800}{90} = 153.3$. This value of n was considerably smaller than the measured value 1399. Taking the above consideration as basis, the reasoning that light and sound were not generated independently in either case seems to be verified. Therefore, some mechanism which accompanies sounding (vibration) should be taken into account as a mechanism of crystalloluminescence.

In order to examine whether such a sounding is observed in substances which present no crystalloluminescence, many experiments were performed, and KNO_3 and K_2SO_4 were found to generate sounds in the course of recrystallization. Figs. 15a, b and 16a, b show the results in cases where 16g of KNO_3 was dissolved in 20cc of water (room temperature 27.15°C) and 7.23g of K_2SO_4 in 31.63cc of water (room temperature 26.55°C), respectively.

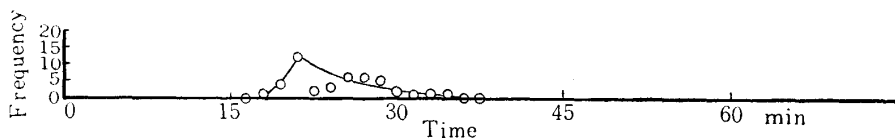


Fig. 15a. Time changes of frequency of sounding per 90 seconds.
Sample: KNO_3 .

* Equation(2) was modified as follows: first, N_L was replaced by N_L' ; and second procedure is mentioned in the following. According to Eq. (3), the frequency of only one light pulse being generated within $(T_L + T_S)$ is N_L''' per second. As considered in the case of Eq. (2), time width of $(T_L + T_S)$ was accompanied by one pulse and so time widths accompanied by $(N_L' - N_L''')$ pulses were overlapped each other. As the degree of this overlapping was variable from zero to T_S , Eq. (4) was derived by taking its mean value $\frac{T_S}{2}$.

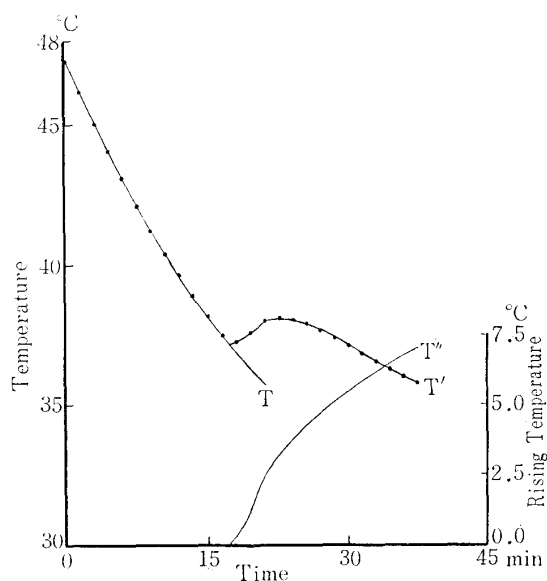


Fig. 15b. Same as Fig. 5b. Sample: KNO_3 .

From this fact it should be noted that the frequency of light pulses was more appropriate than that of sound pulses to be compared with the frequency of coincidence of light and sound pulses.

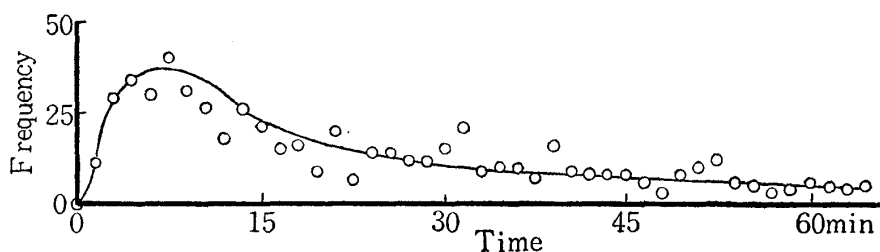


Fig. 16a. Same as Fig. 15a. Sample: K_2SO_4 .

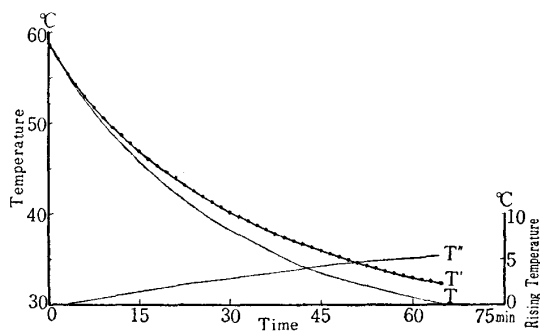


Fig. 16b. Same as Fig. 5b. Sample: K_2SO_4 .

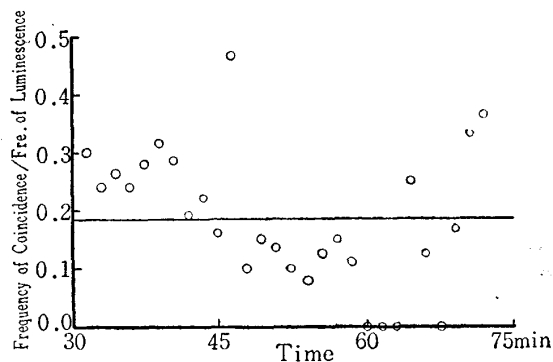
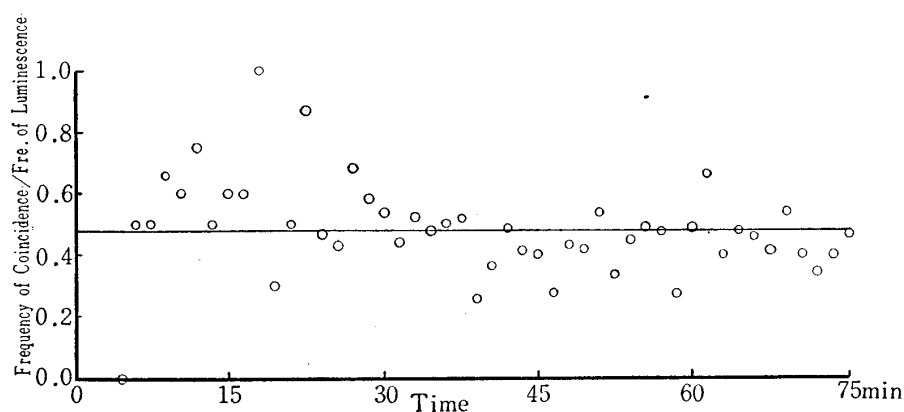
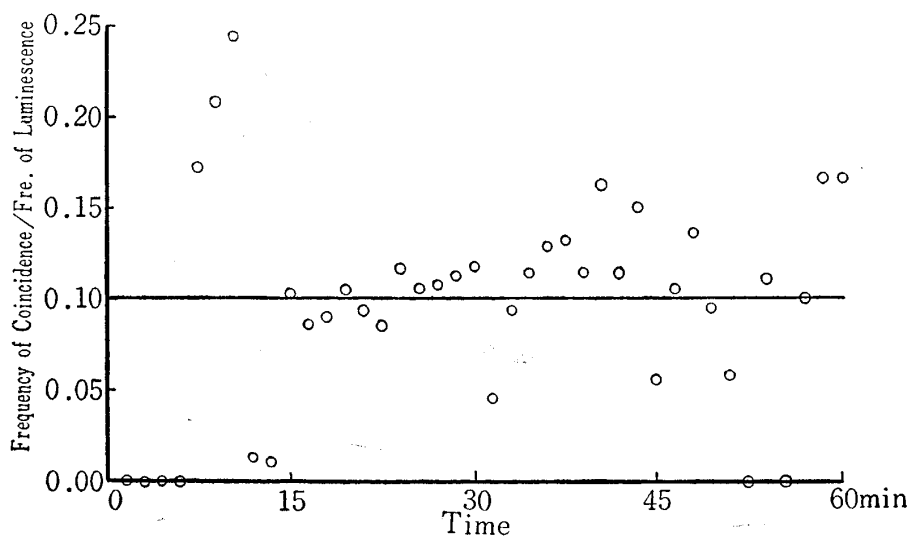


Fig. 17. Time changes of ratio of frequency of coincidental observations to that of light pulses. Sample: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.

Fig. 18. Same as Fig. 17. Sample: $K_3Na(SO_4)_2$.Fig. 19. Same as Fig. 17. Sample: As_2O_3 .

It was preferable to omit the parts where measured values for $Ba(ClO_3)_2 \cdot H_2O$ were very large in this comparison, because in these parts the value of n was small compared with the frequency of coincidental observation but not so small as to be neglected. Ratios of the frequency of coincidental observations to that of light pulses are shown in Figs. 17, 18, and 19, as functions of the lapse of time, where horizontal lines represent the mean values.

Next a consideration will be extended to the temperature in the course of recrystallization. In Fig. 20 is shown a cooling curve when 35cc pure hot water was placed naturally at room temperature $22.25^\circ C$, and the curve looks like a straight line within experimental error. Consequently cooling curves of the solutions (T') shown in Figs. 5b, 6b, and 7b would resemble the curve T , if no latent heat were liberated in the course of recrystallization. (Curves T in Figs. 5b, 6b and 7b were derived from lines T in Figs. 5c, 6c and 7c.)

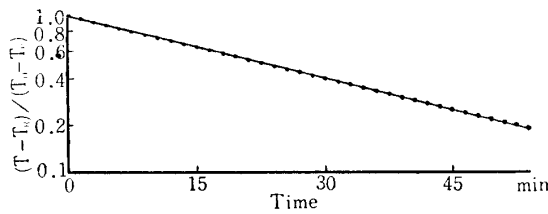


Fig. 20. Cooling curve for pure water.

While the change of temperature is small the amount of crystals recrystallized is proportional to the liberated heat Q accompanying recrystallization, and Q is estimated as follows. The amount of heat which is liberated in time interval dt is expressed by dQ and is represented by

$$dQ_{\infty} = \left(\frac{dT}{dt}\right)_{T'} dt = \left(-\frac{dT'}{dt}\right) dt^*,$$

$$Q_{\infty} = \int_0^t dT' = \sum \left(\frac{dT}{dt}\right)_{T'} dt. \dots\dots\dots (5)$$

Values calculated from the right side of Eq. (5) are represented by curves T'' of Figs. 5b, 6b, and 7b. The same operations were carried out for Figs. 15b and 16b.

The gradients of curves T'' are considered to be proportional to the rates of recrystallization. Furthermore, curves T'' for As_2O_3 and $K_3Na(SO_4)_2$ with crystalloluminescence and K_2SO_4 without it become approximately straight lines and so each of their gradients is nearly constant. From curve T'' for $Ba(ClO_3)_2 \cdot H_2O$ with crystalloluminescence, the fact that the frequencies of both luminescence and sounding became maximum when the rate of recrystallization was the largest can be recognized. Just in the same way as for KNO_3 without crystalloluminescence, the fact that the frequency of sounding became maximum when the rate of recrystallization was at maximum can be seen from curve T'' .

Observing the states of recrystallization for all of the samples used, it was realized that recrystallization began gradually a few or scores of minutes before the measured temperature curve T' began to deviate from the cooling curve T , and that a considerable amount of crystals with a volume less than $1mm^3$ precipitated on the wall of the vessel and on the surface of the solution when luminescence and sounding began to be generated. This indicates that crystalloluminescence and sounding were activated when these small crystals grew rapidly by making themselves their seeds.

Thus the following line of reasoning may be reasonable. All the operations from Experiments (B) to (F) are practically the breaking of crystals. Namely the fact that clear cracks were found in Crystals (b) means that the crystals were broken by Experi-

* $\left(\frac{dT}{dt}\right)_{T'}$ is the gradient of curve T at the same temperature point as a point on the measured temperature curve T' and $\left(-\frac{dT'}{dt}\right)$ is the gradient of curve T' at the same point.

ment (B) and that luminescence at that time may be regarded as triboluminescence. The fact that Crystal (d) was not capable of emitting luminescence in Experiment (D) will be understood by supposing that strains in the crystal was removed by heating and consequently the crystal became less brittle against a breaking force. Similarly it seems natural that Crystal (b) did not repeat luminescence phenomena.

Trautz²⁾ studied triboluminescence concerning number of substances and reported that, though the newly recrystallized crystals were ready to produce triboluminescence, they gradually became harder and finally stopped producing luminescence as time went on. Moreover he found a difference of optical refractive indices between the interior and the peripheral parts of the crystals, and suggested that there were strains inside the crystals. Therefore, it may not be unreasonable to infer the existence of strain in crystals of samples with crystalloluminescence used by the author.

Longchambon³⁾ who regarded crystalloluminescence as one sort of triboluminescence, reported that the luminescence was emitted after recrystallization had nearly completed. However, according to the results of the present experiment, the luminescence was most predominant when the rate of recrystallization was high. The higher is the rate of recrystallization, the more isolation of heat of solution takes place, which causes a vigorous partial rise of temperature of crystals. Thus the crystal comes to be broken by heat because too much strain is accumulated. In this experiment no difference was found regarding the duration of either crystallo- or tribo-luminescence.

Further, when crystals were cooled down very rapidly or shaken violently in the course of recrystallization by cooling, they stopped luminescence. On the other hand, very large crystals produced by very slow cooling did not show crystalloluminescence. The former may be due to the fact that crystals recrystallized were too small to cause non-uniform temperature distribution; and the latter may be due to poor strains in the crystals and small non-uniformity of temperature distribution. Therefore it is necessary to make crystals of an appropriate size with an appropriate rate, as is usually experienced. The reason why the luminescence becomes predominant when the vessel with a considerable amount of crystals is shaken is this: the liberation of latent heat is promoted by accelerating recrystallization and at the same time breaking of crystals is increased by both thermal and mechanical effects.

In the previous section, it was mentioned that $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ which generated crystalloluminescence had the most amount of strains. This agrees with the inference drawn above. Namely crystalloluminescence is regarded as a kind of triboluminescence due to heat of resolution isolated in the course of recrystallization. From this point of view the following will be presumed:

(1) Any substance with crystalloluminescence can emit triboluminescence, that is, it emits light if it is broken by any method.

(2) The reason why KClO_3 does not generate crystalloluminescence may be that it is not broken by the non-uniformity of temperature because its strain is by far smaller than

that of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. However, if it is broken an appropriate way relatively soon after being recrystallized, it can generate triboluminescence. And the above presumptions have been found to agree with the experimental facts.

As is well known, crystals which are capable of emitting triboluminescence are apt to lose the capability with the lapse of time after the preparation of the crystals.²⁾ It was ascertained by the present experiment that strains in crystals of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and KClO_3 which were capable of emitting triboluminescence decreased with the lapse of time.

It has been known that a crystal of NaCl once fused presents predominant triboluminescence, and that pure ZnS does not present luminescence but comes to present it strongly when it is mixed with impurities. These facts seem to be understood by inferring that the existence of strains is necessary for triboluminescence. This agrees well with the fact that if $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{K}_3\text{Na}(\text{SO}_4)_2$ and As_2O_3 which are capable of emitting crystalloluminescence are annealed they become less capable of generating triboluminescence. It can be understood in the same way that NaCO_3 with small strains does not generate triboluminescence.

§ 7. Conclusions and Acknowledgement

The following conclusions will be obtained from the present experiments. By observing the crystals of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{K}_3\text{Na}(\text{SO}_4)_2$, and As_2O_3 , which presented crystalloluminescence, cracks parallel to the planes of cleavage were confirmed in the crystals. The duration of crystallo- and tribo-luminescence was measured and either of their values was found to be less than 10^{-6} sec. Still more the coincidence of luminescence and sounding accompanied crystalloluminescence was detected and it was confirmed that sound was not generated independently of luminescence. Therefore mechanisms of crystalloluminescence should be those which accompany sounding (vibration). By using transient techniques, the free induction decay time T^*_2 for Cl^{35} was measured and it was made clear that there were considerable amounts of strains in samples, i. e., $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and KClO_3 from the behavior of time change of T^*_2 . Since no difference was found between tribo- and crystallo-luminescence, this may be regarded as one sort of that. Namely, crystalloluminescence is to be observed when a large strain in a crystal recrystallized from a solution at an appropriate rate is removed, with the crystals destroyed, by the heat generated in the course of recrystallization. Therefore it is natural to conclude that crystalloluminescence should be one sort of triboluminescence.

The author wishes to express his appreciation to Professor Takeo Fujiwara and Professor Haruo Takeyama of Hiroshima University for their encouragement and guidance throughout this research.

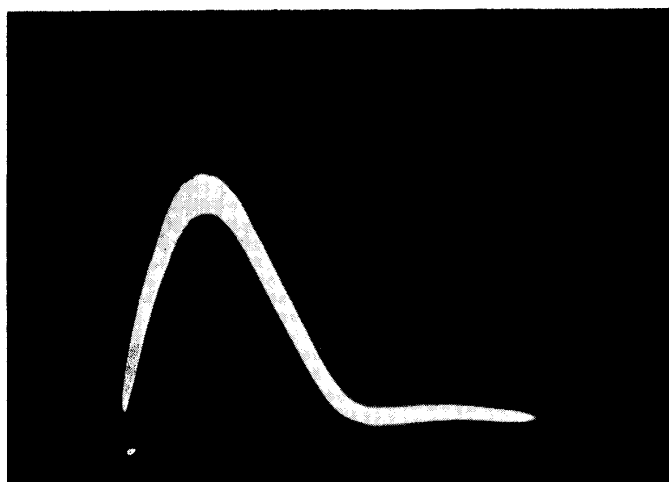


Fig. a. Photocurrent, the duration of which is 4.2×10^{-6} sec.

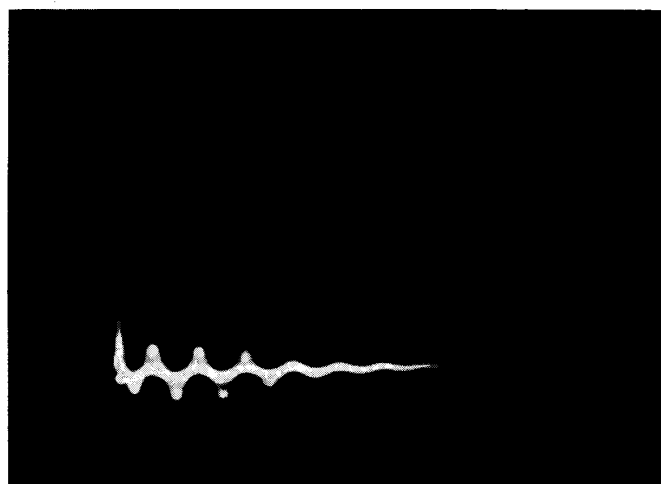


Fig. 2b. A. c., frequency of which is 1.22 Mc/sec.

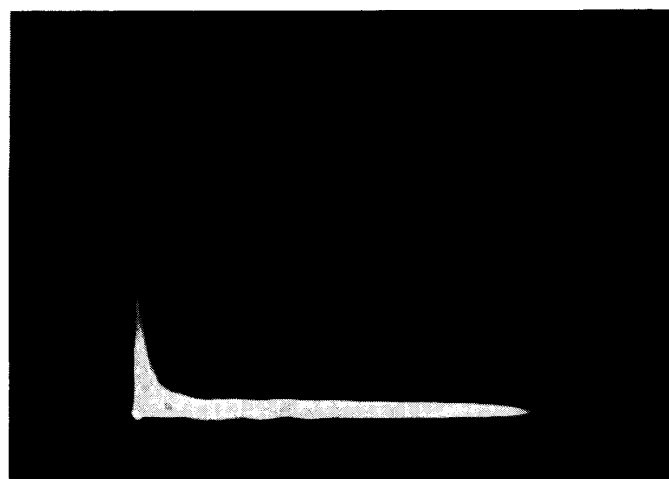


Fig. 2c. Photocurrent of crystalloluminescence.
Sample: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.

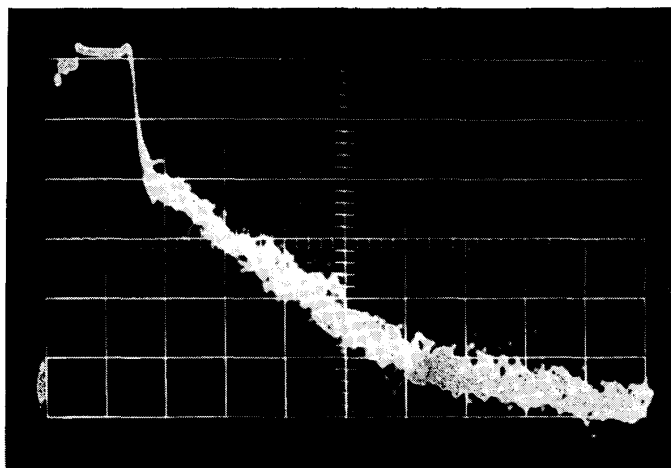


Fig. 11. Oscillographic display of the free induction signal due to Cl^{35} in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ crystals at 29.4Mc/sec. Full scale is 300μ sec. $T^*_2 = 8.5 \times 10^{-5}$ sec.

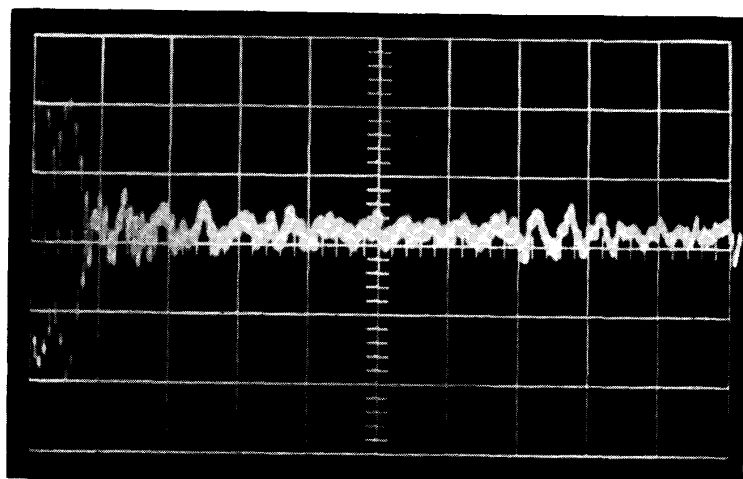


Fig. 14. Oscillographic display of a sound accompanying crystalloluminescence. Full scale of the horizontal axis is 10 m sec. and the duration of sound is about 0.8 m sec.
Sample: $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.

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