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EFFECTS OF PLASTIC DEFORMATION ON THE PROPERTIES OF
SCINTILLATION OF NaI(Tl) CRYSTAL

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The large single crystals of NaI(Tl) were produced by Stockbarger's and Kyropoulos' methods. The most adequate conditions for the growth of these crystals were studied. The thallium distributions in the crystal were measured, and the relation between the photon yield in the scintillation and the thallium concentration was also studied. On the other hand, the effects of the plastic deformation on the decay time and on the photon yield in NaI(Tl) scintillation were measured, and the reasonable models being responsible for the luminescent center of scintillator were discussed.

Introduction

Many researches have been done in order to enable thallium activated alkali halide single crystals to use as scintillator. In these scintillators, especially NaI(Tl), KI(Tl) and CsI(Tl) being produced by various methods have been investigated about their fundamental properties because of their usefulness as the scintillator. NaI(Tl) single crystal is very difficult to produce because of its properties which are hygroscopic, chemically unstable and feeble for thermal and mechanical shock.

The procedure of growth of these crystals should be analysed considering their properties as scintillator, which are expressed to be low background, to have the good photon yield per unit incident radiation energy, and to have the good resolution for incident radiation energy.

Producing these crystals after Stockbarger's and Kyropoulos' methods, the author investigated the relations between the growth conditions and the properties of these crystals as scintillator. The scintillation phenomena under various conditions were surveyed to explain the mechanism in scintillation process with high energy radiation.

On the other hand, the temperature dependence of the emission spectrum of NaI(Tl) scintillation and the pressure dependence of the absorption spectrum of thallium ion were measured by Van Sciver¹⁾ and Drickamer²⁾. From the results obtained, the scintillation mechanism is explained following Williams-Seitz model^{3,4)} except for the energy transfer process from the crystal lattice to luminescent centers. From the other standpoint, the scintillation mechanism is also explained in terms of the assumption that the luminescent center should be originated in the thallium-halogen

1) W. Van Sciver, *IRE Trans. on Nuclear Science*, NS-3, 39 (1956)2) R. A. Eppler and H. G. Drickamer, *J. Phys. Chem. Solids*, 6, 180 (1958)3) F. Seitz, *J. Chem. Phys.*, 6, 150 (1938)4) P. D. Johnson and F. E. Williams, *ibid.*, 18, 1477 (1951); 19, 457 (1951); 21, 125 (1953); *Phys. Rev.*, 82, 281 (1951); 84, 1181 (1951)

complex.^{5,6,7)}

The effects of the plastic deformation of NaI(Tl) on the scintillation spectrum with Cs¹³⁷ gamma-rays and on the decay time were measured, and the scintillation mechanism was discussed from the results obtained and some optical data for the crystal with plastic deformation.

Experimental

The raw materials to produce NaI(Tl) single crystal were prepared by the purification of the commercialized reagent with the highest purity. The reagent of NaI contains NaOH and Na₂O *etc.* by their hydrolysis and Na₂CO₃ introduced during their process of synthesis. The ingots produced from the reagent unpurified were cloudy in appearance and inadequate to take optical data. Consequently, the reagent was recrystallized in the methyl alcohol solution, and then dried at the high temperature, 500°C, and at the reduced pressure. The reagent was purified by the treatment in H₂ and I₂ vapours being deoxidized and dehydrated. The mixtures of 0.8~1.2 weight % TlI powder into the purified mother reagent were used to produce the single crystal by Kyropoulos' and Stockbarger's methods.

The crucibles used as the vessel of the crystallization were made of glass, fused silica, porcelain, graphite, platinum and alumina, and the most adequate material for the crystal growth was examined. The growth of the crystal was operated in the air, N₂ and He gases, or at the reduced pressure.

The effects of the growth conditions, such as the temperature distribution in the furnace, the pulling-up rate of seed crystal in Kyropoulos' method and the lowering rate of the crucible in Stockbarger's method, on the crystal properties as scintillator were surveyed. Also these growth conditions have influence upon the thallium distributions in the crystals which have the effects on the properties of the scintillation. So the thallium distributions in these crystals were measured by the spectrophotometric analysis employing the Hitachi EPV-2 Spectrometer by which the thallium concentrations were decided by the absorption band at 400 m μ due to thallium-oxinate.

The samples (about 30×10×10 mm) were plastically deformed uniaxially to the deformation ratios expected with a pressure of about 2000 kg/cm². The apparatus used to deform the crystal is shown in Fig. 1.

On the other hand, the photon yield per unit incident radiation energy in scintillation is the functions of the thallium concentration in NaI(Tl) and of the deformation ratio in the case of plastically deformed NaI(Tl) crystals. The photon yields in this experiment were expressed at the pulse heights by converting the photons in scintillator to the electronic pulse using the EMI 6097 F multiplier phototube.

The scintillation spectra of these crystals irradiated with Cs¹³⁷ gamma-rays were measured by

5) S. Makishima, S. Hayakawa and T. Tomotsu, *Nippon Butsuri Gakkai Shi*, **14**, 402 (1959)

6) K. Ozawa, *Bull. Inst. Chem. Res. Kyoto Univ.*, **37**, 327 (1959)

7) W. J. Fredericks and A. B. Scott, *J. Chem. Soc.*, **28**, 249 (1958)

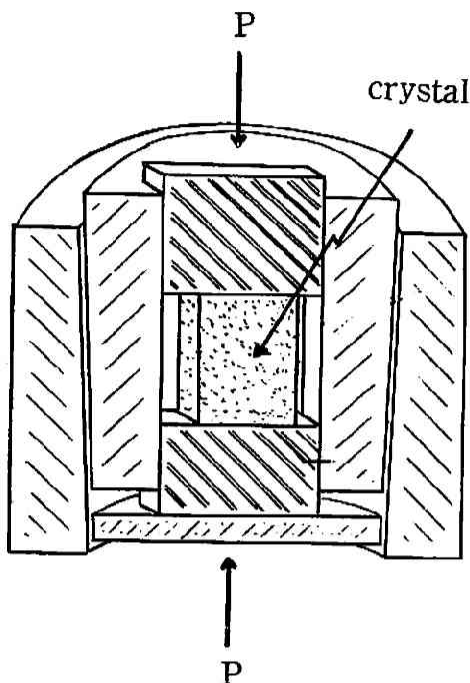


Fig. 1 Schematic diagram of apparatus used to deform crystals

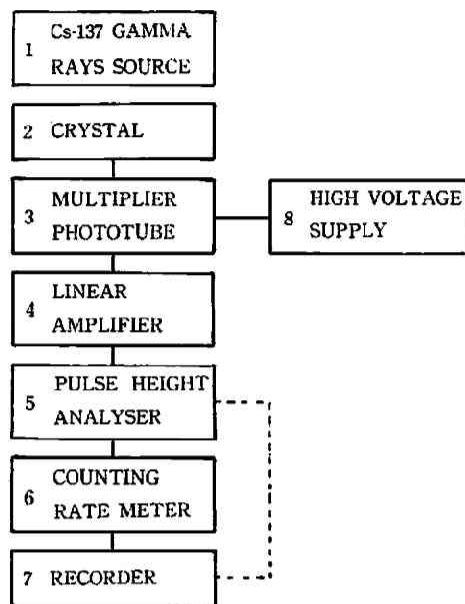


Fig. 2 Block diagram of single channel pulse height analyser

HRL Single Channel Pulse Height Analyser SS-1 with the block diagram shown in Fig. 2.

The decay times of the scintillation which are dependent on the deformation ratios of the crystals were measured as the electronic pulse decays from the multiplier phototube using the Oscilloscope Tektronix 545.

Results and Discussion

1 Crystal growth The atmosphere in contact with the liquid phase of NaI in crystallization should be N_2 or He gas to obtain a good transparent single crystal. The injection of cloudy parts into the crystal could be avoided by making the temperature gradient larger as possible in the liquid phase near the solid-liquid surface of NaI. The cloudy parts in the crystal as grown may be impurity, possibly NaOH or $Na_2O^{8,9}$.

From the reason mentioned above, Stockbarger's method was recommendable to obtain a large transparent single crystal of NaI(Tl). The most adequate crucible was made of platinum because of its heat- and corrosion-proof.

2 Thallium distributions in NaI(Tl) single crystal The thallium distributions in NaI(Tl) crystals obtained by Stockbarger's and Kyropoulos' methods are shown in Figs. 3 and 4

8) L. M. Belyaev, V. P. Panova, V. A. Perischtein, V. V. Chadaeva and I. N. Tzigler, *Izv. AN SSSR. Ser. Fiz.*, **22**, 21 (1958)

9) L. M. Schamovskii, L. M. Radinova and A. S. Gluschkova, *ibid.*, **22**, 3 (1958)

respectively. The theory on the impurity distribution in the crystal has been proposed by McFee¹⁰⁾ with the several assumptions in the case of Stockbarger's method. On this theory, the following equation has been established;

$$C/C_0 = A(1-h/H_0)^{A-1}, \quad (1)$$

where C_0 is the concentration of thallium ions initially present in atomic percent thallium ion to sodium ion; C , the concentration of thallium ion in the position at a height, h , from the crystal bottom in the same meaning mentioned above; A , the constant of proportionality or purification constant; and H_0 , the total height of ingot from 2/3 of cone type part. Comparing the theoretical

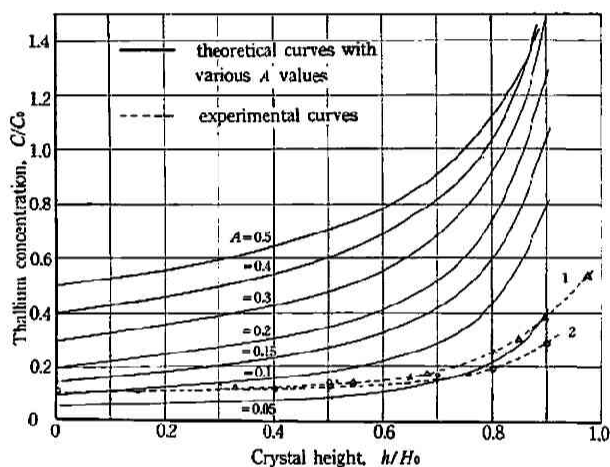


Fig. 3 Experimental and theoretical relations between thallium distributions and crystal heights of NaI(Tl) in which experimental curves 1 and 2 are taken from crystals of growth rates 0.6 and 1mm/hr respectively (Stockbarger's method)

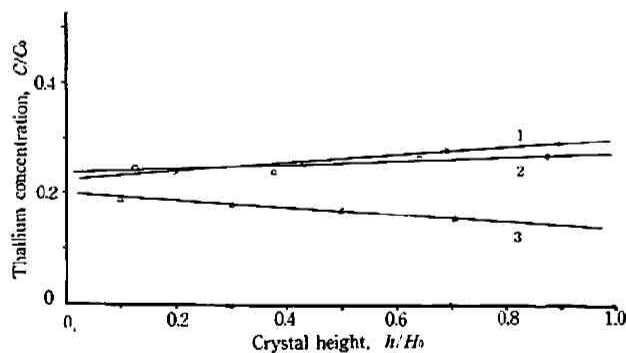


Fig. 4 Experimental relations between thallium distributions and heights of NaI(Tl) crystals whose growth rates are 1.7, 2.6 and 2.8 mm/hr for curves 1, 2 and 3 respectively (Kyropoulos' method)

curves of the thallium concentration with the experimental curves shown in Fig. 3, a serious deviation between them was found. This deviation is considered to be due to the result of the unconstancy of the purification constant, A . Namely, the A values estimated from the experiments varied with the crystal heights. On the other hand, the above Equation (1) is founded on the following equation:

10) R. H. McFee, *J. Chem. Phys.*, **15**, 856 (1947)

$$a_A = Ab_A, \quad (2)$$

where a_A is the concentration of impurity ions in the crystal at a height, h , and b_A is the concentration of impurity ions in the melt at the point when the crystal has grown to a height, h . The A values obtained from the experiments were larger in early stages of the crystal growth than in final stages. Thus, it was concluded that thallium ions are distributed into the NaI crystal in the different manner from that mentioned by the above theory. It is supposed that the thallium ions are injected into NaI crystal lattice in the state, such as the thallium-halogen complex, of which the potential energy is lower than that of the isolated ion.

3 Relations of thallium concentrations in NaI(Tl) and photon yield in scintillation By the method used in this experiment for estimating the photon yield in scintillation, the absolute number of photons can not be easily estimated. However, the curve of the photon number vs. the pulse height is shown to be exactly linear in the wide range. Consequently the comparison of the relative photon yields by using the pulse height method can be thought to be an exact method. The relations between the pulse heights and the thallium concentrations in NaI(Tl) are shown in Fig. 5, but this result differs from the result of Harshaw *et al.*¹¹⁾, in which the pulse heights linearly increase depending on the TII concentrations until they reach to 0.1 weight per cent, and saturate in the range beyond 0.1 weight per cent.

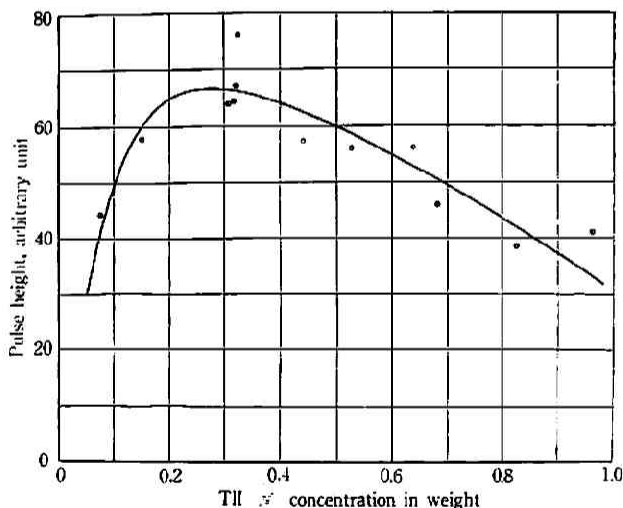


Fig. 5 Relation between thallium concentrations and photon yields expressed as pulse height in NaI(Tl) crystal irradiated by Cs^{137} gamma-rays

On the other hand, in the case of KCl(Tl) the similar result shown in Fig. 5 has been reported by Johnson and Williams¹²⁾, and the following theory about the photon yield has been proposed to explain their result,

$$\eta = \frac{C(1-C)^2}{C + (\beta/\alpha)(1-C)}, \quad (3)$$

11) J. A. Harshaw, H. C. Kremers, E. C. Stewart, E. C. Warburton and J. O. Hay, *AEC Report NYO-1577* (1952)

12) P. D. Johnson and F. E. Williams, *J. Chem. Phys.*, 18, 1477 (1950)

where η is photon yield per incident radiation energy; Z , the potassium ion number existing in the sphere whose diameter, R , is given; C , the probability of the occupation by the thallium ion in the site of potassium ion; and β/α , the ratio of cross sections of the lattice atom and the thallium for the exciting radiation.

The foundation of this theory was established on an assumption that the increase of the probability of the existence of thallium ions close to each other by the some excess of thallium concentration, may cause suppression to form the luminescent center. The same discussion can be also applied to the case of NaI(Tl). Introducing the assumption that the luminescent center may be the thallium-halogen complex, the interaction of the thallium ions to each other can be understood as follows: the electron orbitals of the activated state of the thallium ions are widely spread over the neighboring crystal lattice, especially to the electron orbitals of the halogen ions at the nearest neighbor, and then the over-lapping of the electron orbitals restrict the formation of luminescent center of free thallium ion.

4 Effects of plastic deformation on decay time and photon yield in scintillation of NaI(Tl) The single crystals (about $30 \times 10 \times 10$ mm) of NaI(Tl) were plastically deformed uniaxially and the effects of the deformation on the decay time and the photon yield expressed as the pulse height are listed in Table.

As shown in Table, the pulse heights are decreased and the decay times are increased with increasing the deformation ratios of crystals. The reason of the decreasing of the pulse height is

Table Effects of deformation on pulse height and decay time*

Crystal No.	Deformation ratio, %	Pulse height (Relative)	Decay time (Relative)
1	6.5	100	100
2	13.0	91	122
3	19.5	84	134
4	26.0	79	143

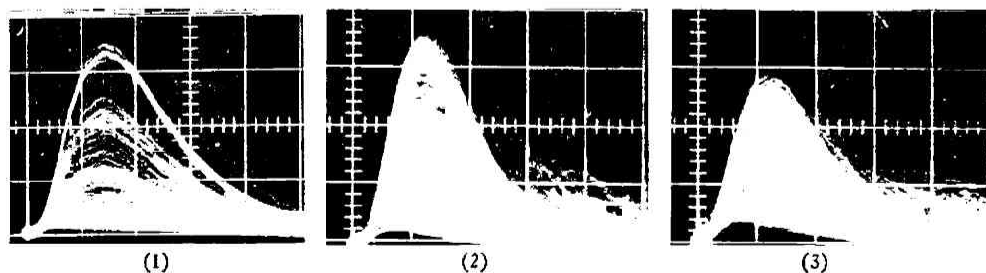


Fig. 6 Photographs of oscilloscope showing decay of NaI(Tl) scintillation (1) not deformed, (2) deformed by ratio 6.5% and (3) 19.5%, in which high voltages given on multiplier phototube are 800V for (1) and 1100V for (2) and (3) respectively (Ordinate; 0.2μ sec per division. Abscissa; $5/30V$ per division)

* In this Table, the standards of the pulse heights and the decay times are taken on the deformation ratio of 6.5%.

supposed as follows; (1) the increase of the number of the traps for the excitation energy conveyers, such as electrons, holes or excitons, (2) the increase of the radiationless transitions from the excited states of the luminescent centers to the ground state, and (3) the decrease of the optical yield of photons arrived to the photocathode for generated photons.

On the other hand, the increase of decay time may be the results from the relaxation of the excited state in scintillation for the ground state by the deformation of crystals. And then the difference in the types of decay time could not be found in the curves shown in Fig. 6.

5 Effects of plastic deformation on resolution in scintillation spectra The effects of the plastic deformation with 50% of the ratio on the scintillation spectra of NaI(Tl) excited with the Cs^{137} gamma rays were measured and the typical result is shown in Fig. 7. The

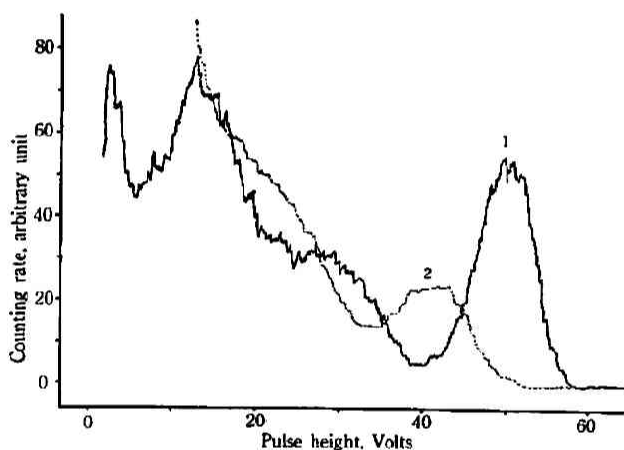


Fig. 7 Scintillation spectra of NaI (Tl) crystal irradiated by Cs^{137} gamma-rays; 1, not deformed, 2, deformed of ratio 50%; ratio of amplification of 1 to 2 is about 3.4.

bands which show the photopeaks in these spectra were broadened by the deformation. The ratio of the half width of the band to the pulse height of the center of the photopeak is defined as the resolution in the scintillation spectra. The resolution, R_{obs} , observed by using scintillation spectrometer is separated into two parts, based on the following relation, $R_{obs}^2 = R_{int}^2 + R_{res}^2$, one part is due to the intrinsic of the scintillator, R_{int} , and the other, R_{res} , due to the measuring system itself. Thus, the increase of the spread of R_{obs} is only originated in the increase of R_{int} . On the other hand, the spread of R_{int} , is partly originated in the statistical fluctuation in each process of the scintillation, so that the decrease of the photon yield by the deformation mentioned above causes the increase of the statistical fluctuation in each scintillation process. And then the increase of the number of luminescent center by the deformation may also cause broadening the spread of the R_{int} .

6 Reasonable model being responsible for luminescent center Recently, Abdusadykov¹³⁾ has reported that a new type of luminescent centers in KCl(Tl) was generated not only by the increases in the concentration of activator in host crystal, but also by the plastic deformation of crystal with low concentration of activator, which is identical in general aspect

13) T. Abdusadykov, *Optica i Spektroskopii*, 7, 158 (1959)

with a high concentration of the dislocations and vacancies in the crystal lattice. The centers whose emission bands were at 380 and 485 m μ were assumed to be the complexes of ions of the activator and the small defects of the host lattice.

On the other hand, it is newly found¹⁴⁾ that an absorption band in infrared region is induced at around 1620cm⁻¹, when the crystals of KI(Tl) are plastically deformed. This new band may be also probably due to the complexes of the impurity ions and the vacancies or the dislocations generated by the deformation. As shown in sections 1~5 in this chapter, the electron orbitals of the excited states of the luminescent center are thought to be widely spread to the neighbouring ions, when the crystals are deformed plastically or activated by the excess of thallium.

Williams and Seitz^{3,4)} considered that the activator ions of the luminescent center in alkali halide are isolated from the neighbouring ions, and that the excited electrons are bound strongly to the activator atom. From another standpoint^{5,6,7)}, the origin of the luminescence is also considered to be thallium-halogen complex. But the actual state of the luminescent center is supposed to be the intermediate state between the isolated thallium ion and the thallium-halogen complex. In other words, the luminescent centers in nearly perfect crystal can be considered to be isolated from the neighbouring ions, and in the crystal deformed plastically or containing of the excess of activator, the centers capture the defects generated by these treatments, and their electron orbitals are widely spread to the halogen ion.

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14) K. Ozawa and M. Ōura, to be published in *This Journal*