Effects of Gamma-Radiation on Alkali Halide Crystals

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The radiation effects by γ-rays on the infrared absorption spectra of alkali halide crystals (LiF, KI-Tl, and NaI-Tl) have been investigated. In LiF crystal, the 3595 cm^{-1} band caused by FH$\cdots$F anions has vanished completely at 4.4×10^6 r, but the new absorption bands appeared at around 1950 cm^{-1}. In KI-Tl crystal, the new absorption bands at around 1410, 1370, 888, and 805 cm^{-1} which should not appear in nominally pure KI crystal have been observed. The absorption bands at around 1370 and 805 cm^{-1} were decreased and a new induced band at around 1250 cm^{-1} was enhanced with increasing dosage of γ-rays. Similar spectra are obtained by NaI-Tl crystal. On the other hand the data on the pressure dependence of the dielectric constant of NaCl irradiated with γ-rays are given as a function of hydrostatic pressure from 0 to 5,000 kg/cm^2.

INTRODUCTION

The defects in crystals can be produced in appreciable concentration by means of mechanical work, radiation, and addition of chemical impurities. This paper is concerned with the optical and electrical properties of alkali halide crystals after they have been irradiated with γ-rays. This work is part of a program of study of the imperfection in alkali halide crystals[1].

Hersh[2] has recently studied the color centers in KI-Tl after x-raying and suggested that Tl$^+$ ions act as electron traps and F-bleaching at room temperature of x-rayed crystals results in the formation of vacancy aggregates which are related to the production of halogen centers, and he has detected iodine in aqueous solutions of crystals which have been previously x-rayed and optically bleached, and no iodine in solutions of unirradiated crystals.

On the other hand, Mayburg[3] has measured the pressure dependence on the low frequency constant of alkali halide crystals up to 8,000 bars, and shown that they are reduced with increasing pressure.

In this paper the natures of the defects in alkali halide crystals produced by the application of hydrostatic pressure, γ-ray irradiation, and the addition of impurities, are investigated by means of infrared absorption and dielectric constant.

EXPERIMENTAL PROCEDURE

In this work the single crystals of LiF, NaCl, and KI-Tl and NaI-Tl activated with Tl$^+$ ions of the content of about 10^{-3} to 10^{-2} mole percent were employed. KI-Tl and NaI-Tl crystals were produced by Stockbarger's method of lowering

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a pointed bottom crucible along the axis of vertical tubular furnaces. The other crystals were produced by the modification of Kyropoulos' method of growing the cooling seed in the melt. The experimental samples were prepared by cleaving thin specimens from large single crystals, usually about 10×20 mm^2 in area and $5 \sim 10$ mm thick for the optical measurements and 16×12 mm^2 and 1.5 mm for those of dielectric constant at high pressure. NaI–Tl crystal which has a hygroscopic nature was mounted by a method of Al canning obtaining a sandwich seal employed Al ring and two plates of NaCl crystal.

The irradiation on crystals was performed by γ-rays $(2.3 \times 10^5$ r/hr) from Co^{60} of 1,940 Curies in the Institute for Chemical Research of Kyoto University. The infrared spectra were obtained using a Perkin Elmer Model 21 spectrometer with NaCl optics. For the measurement of dielectric constant at high pressure, the pressure bomb with four electrodes and one stop valve which is connected to an intensifier was constructed. The schematic diagram is shown in Fig. 1. The
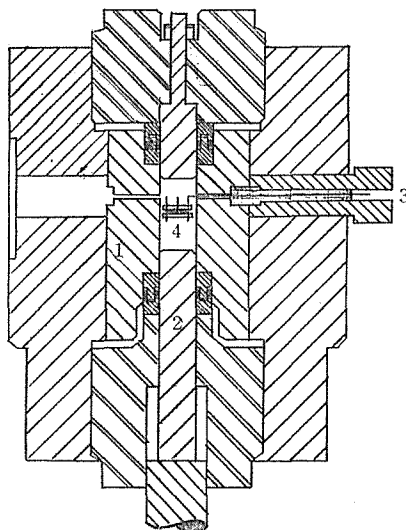

Fig. 1. The pressure bomb for dielectric measurement.
　1 : pressure-proof cylinder of 20 mm inner diameter
　2 : moving piston connected to intensifier
　3 : electrode
　4 : sample

main problem was to seal an electrical lead into the high pressure bomb. The sealing was performed by the unsupported area principle. The high pressure electrode was satisfactory for measuring the dielectric constant up to 5,000 kg/cm^2. The resistance pressure gauge using manganin wire was designed for measuring pressure. The pressure fluid was silicone liquid. The dielectric constant was measured with an impedance bridge of parallel resistance type at 1,000 c.p.s. A thin specimen of crystals covered with vaseline was held between guarded and unguarded electrodes, Al 30μ thick, which were stuck on the plastic plates. Three electrical leads of 0.8 mm in diameter and 25 mm in length soldered with the electrodes acted both as electric connection to the high pressure

electrodes and as supports. The actual geometry is also shown in Fig. 1:

RESULTS AND DISCUSSIONS

A. Infrared Absorption Spectra of Alkali Halide Crystals Irradiated with γ-Rays

1. **LiF crystal.** LiF single crystals grown in air, using the method of Kyropoulos show a prominent infrared absorption at around 3595 cm^{-1}. The band is very much weaker in all vacuum-grown crystals, but does not vanish completely. It is surmised that the 3595 cm^{-1} band is caused by F-H or O-H stretching vibration in a complex with hydrogen bonds of F-H···F or O-H···O anion, which are produced by the hydrolysis of LiF salt in the crystals[4,5]. The existence of 3595 cm^{-1} band for the infrared transparent materials is definitely an imperfection in the air-grown LiF crystals. However, if these LiF crystals with 3595 cm^{-1} band are exposed to γ-rays, differences in the infrared absorption band are detected. Fig. 2 shows the infrared absorption spectra of a LiF crystal, before it was irradiated, and after it had received 1.7×10^6 r and 4.4×10^6 r of γ-radiation respectively. The 3595 cm^{-1} band diminished and finally vanished completely, but on the other hand a weak absorption band was enhanced at around 1950 cm^{-1} with increasing dosages of γ-rays. Both bands show a quantitative change with a finite dosage of γ-rays.
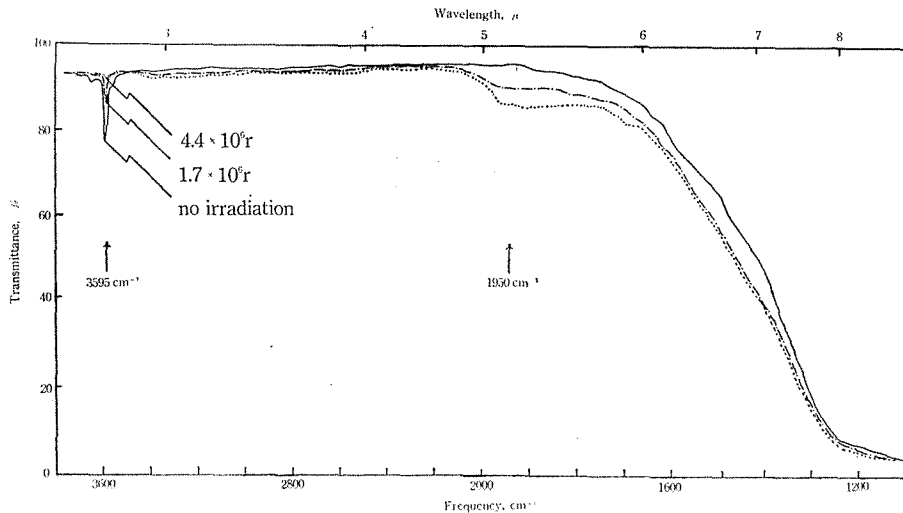

Fig. 2. Effect of γ-ray irradiation in infrared absorption spectra of LiF crystal.

The result would be considered as follows. Generally, the stretching band of hydrogen bond in a complex shifts to lower frequency with decreasing hydrogen bond length. The large frequency displacement and the breadth of the bands are shown by the coordination of a complex with hydrogen bond to a metal[6]. The irradiation produces free anions as the result of the breaking of the complex with hydrogen bonds which contribute to the 3595 cm^{-1} band, and on the other hand produces lithum metal and other impurity metals as the

result of electron capture by metal ions. The free anions coordinate with the metal and precipitate a new complex, such as metal-$(HF_2)_n$. The short and strong hydrogen bonds are constituted in the new complex and the vibration contributes to the broad band at around 1950 cm^{-1}.

2. **KI-Tl and NaI-Tl Crystal.** It is well known that KI, NaI, and TlI crystals are useful transmitting materials in the infrared region. However, it was newly found that the single crystals of the iodides of sodium and potassium activated by thallium impurity are accompanied by some absorption bands in the infrared region. The observed values of the frequencies associated with the peaks in absorption bands of both crystals are given in the Table.

Table Vibration frequencies of KI-Tl and NaI-Tl.

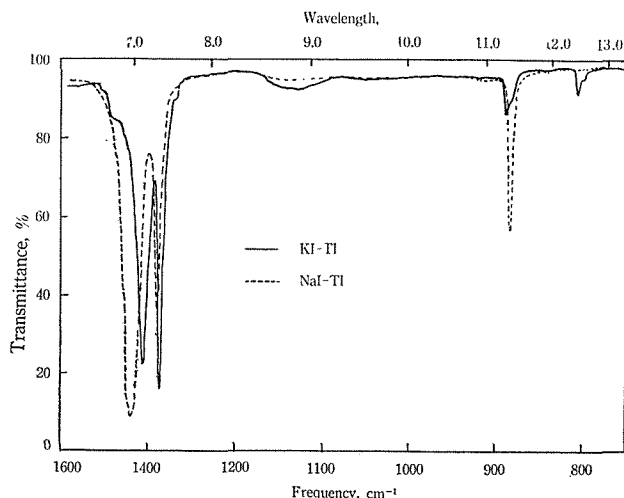| Crystals	Wave numbers at absorption peak (cm^{-1})			
KI-Tl	1410	1370	888	805
NaI-Tl	1438	1375	883	—

Fig. 3. Infrared absorption spectra of KI-Tl and NaI-Tl crystals.

These are shown in Fig. 3 for both crystals of KI-Tl and NaI-Tl. In the case of NaI-Tl the band at around 800 cm^{-1} is not present and there is a band at 3595 cm^{-1} which indicates O-H stretching frequencies of the very little hydrogen bonding attached on the crystal surfaces.

When both crystals are exposed to γ-radiation, an absorption band similar to the 1950 cm^{-1} band observed in LiF crystal is induced at around 1250 cm^{-1}. The most interesting feature is the production of a newly induced band at 1250 cm^{-1} with the reduction of the absorption bands at around 1375 cm^{-1} and 805 cm^{-1} (except NaI-Tl) approximately linear with the radiation dose. Fig. 4 shows the infrared absorption spectra for KI-Tl crystal with 5.5 mm thickness by
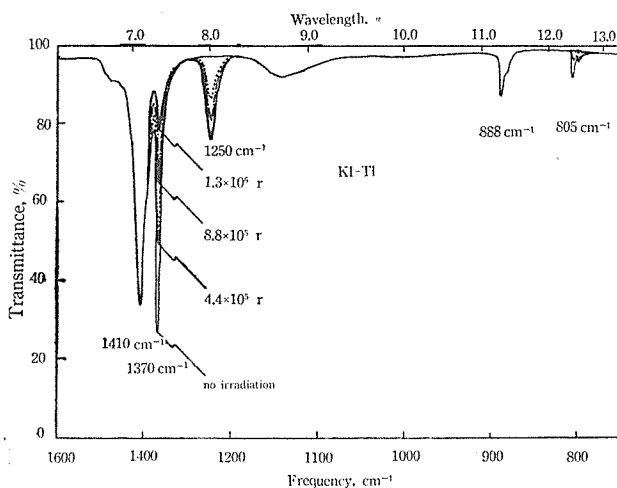
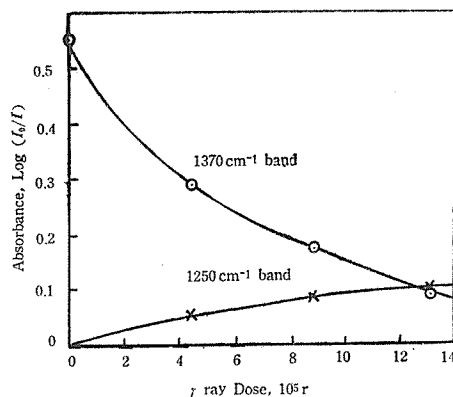Fig. 4. Effect of γ-ray irradiation in infrared absorption spectra of KI–Tl crystal.

Fig. 5. Absorbance *vs.* dose curve for the bands of 1370 cm^{-1}
and 1250 cm^{-1} of KI–Tl crystal.

dosages of 4.4×10^5 r, 8.8×10^5 r, and 1.3×10^6 r respectively compared with a spectrum of virgin crystal. The growth at the peak of 1250 cm^{-1} band and the diminution at 1370 cm^{-1} produced by irradiation are shown in Fig. 5. A similar mutual interconversion of 1375 cm^{-1} and 1250 cm^{-1} bands due to γ-ray irradiation could be also observed for NaI–Tl crystal. This induced band at 1250 cm^{-1} diminishes and both the 1375 cm^{-1} and 805 cm^{-1} bands recover with their original intensity if the crystal is annealed at high temperature. Fig. 6 shows the absorption spectra of a KI–Tl crystal exposed by about 1.4×10^7 r with γ-rays, before and after this crystal has been subjected to the annealing at about 400°C. This figure also shows the spectrum of a sample reirradiated by 7.7×10^6 r with γ-rays, after the crystal has been subjected to the thermal annealing, which is approximately the same as that obtained with a virgin sample irradiated with γ-rays. However, the intensities of both 1410 cm^{-1} and 888 cm^{-1} bands are not changed by the irradiation of γ-rays. Thus, it is thought that there is an equilibrium relation between the 1370 cm^{-1} band and the induced band at 1250 cm^{-1}.
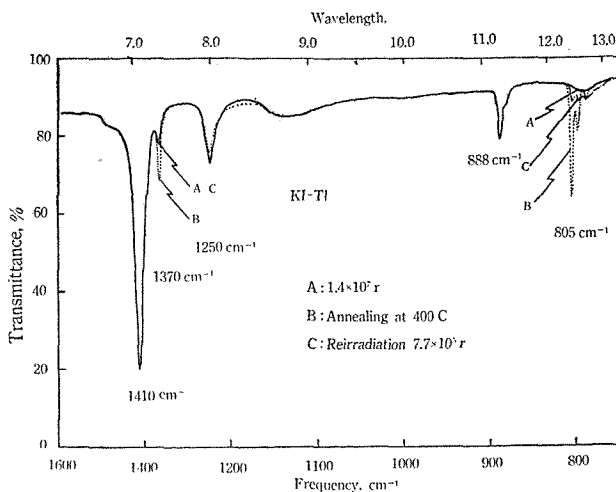
Fig. 6. Effects of annealing and reirradiation in infrared absorption
spectra of KI-Tl crystal.

For the model responsible for luminescence in alkali halide thallium activated
phosphors, Seitz[7] and Williams et al.[8] have postulated these centers responsi-
ble as simple Tl+ ions which occupy lattice sites normally occupied by alkali
metal ions. However, one should not expect to observe the infrared absorption
spectra indicating complex molecular vibrations from the Seitz and Williams
model. Recently, Knox, and Dexter[9] have computed the free-ion oscillator
strengths for the KCl-Tl center of Seitz-Williams model and pointed out that
the results were in poor agreement with experimental f values in the solid and
their model should not be considered. On the other hand, Scott et al.[10] prov-
ed that lead ions in solid KCl exist in the form of the anionic halogen com-
plexes such as $PbCl_6^{-4}$ not as simple ions by the transference experiments on
Pb in KCl crystal and suggested the probability that thallium ions in solid are
also bound in the negatively charged complex at room or lower temperatures;
and Scott et al.[11] demonstrated the presence of $TlCl_2^-$ in KCl solutions contain-
ing a small amount of TlCl. Makishima et al.[12] reviewed the evidence that
luminescence and absorption in the solid phosphors are also due to "complex
centers" which are produced by charge transfer proceses of $X^- \rightarrow Tl^+$. Hersh[2]
has also demonstrated the appearance of the characteristic iodine bands due
to a complex of thallium and iodine which is possibly the TlI_4^- ion[13,14] in the
solid as a result of x-irradiation.

On the other hand, γ-rayed KI-Tl crystals appear bluishgreen rather than
blue as in nominally pure KI and upon being exposed to white light the
crystal loses all of its blue-green color in a few seconds and turns yellow-
orange, which suggests the formation of halogen centers. Thus, the centers
responsible for absorption and luminescence in KI-Tl and NaI-Tl should be
considered as anionic halogen complexes of the thallium metal and of the
other impurity metals introduced into the crystal melt. The further experi-
mental and theoritical investigations are necessary to make clear the nature

and the assignment of the infrared absorption bands and the roles of impurities in the kinetics of band formation.

B. Pressure Dependence of Dielectric Constant of NaCl Crystal Irradiated with γ-Rays

Fig. 7 shows the results of the measurements for pressure dependence up to 5,000 kg/cm² of the dielectric constants of NaCl crystals which received a total dose of 1.1×10^7 r γ-rays and of the orginal samples. The dielectric constant of NaCl crystal at atmospheric pressure are decreased by radiation and they are directly reduced with increasing pressure. The pressure dependences of the dielectric constants, $-(\partial \varepsilon / \partial P)_T \times 10^{-4} (\text{kg/cm}^2)^{-1}$, are 1.12 for as grown and 2.37 for irradiated crystal, respectively.
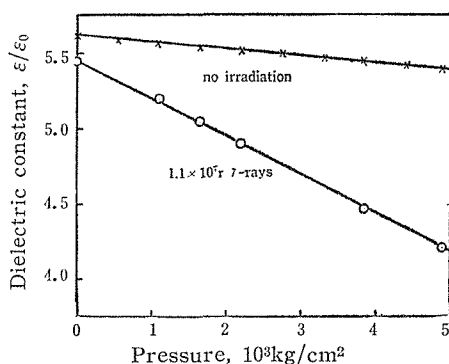

Fig. 7. The pressure dependence of the dielectric constants of NaCl crystal irradiated by γ-rays.

It can be concluded that the pressure dependences of the dielectric constants increase more rapidly in the irradiated crystal. Mott and Littleton[15] have derived the equation,

$$\frac{\varepsilon - 1}{4\pi} = \frac{8\pi \beta \beta_0 (\gamma - 1)/3 + (\beta + \beta_0)}{1 - 4\pi(\beta + \beta_0)/3 + 16\pi^2 \beta \beta_0 (1 - \gamma^2)/9} \text{ ,} \tag{1}$$

where ε is the dielectric constant, β_0 is the polarizability of the electrons of the ions per unit volume, β is the ionic polarizability per unit volume, and γ is the constant of the inner field. The value of the constant γ is defined as follows:

$$F = E + \gamma \frac{4}{3} \pi P, \tag{2}$$

where F is the effective polarizing field, E is the external electric field, and P is the total polarization per unit volume. The relation between the ionic polarizability, β, and the repulsive overlap force constant, R, is

$$\beta = N(Ze)^2/R, \tag{3}$$

where Ze is the ionic charge and N is the number of ion pairs per unit volume. For the NaCl type lattice, the relation between the force constant, R, and the external pressure, P, is

$$R = 6a/x - 8Pa, \tag{4}$$

where a is the lattice constant and x is the compressibility. The increase of the external pressure makes the ionic polarizability, β, decrease from Eq. (3), according to the increase of the force constant, R, from Eq. (4). The decrease of the ionic polarizability, β, is ascribed to the decrease of the dielectric constant from Eq. (1).

On the other hand, Yamashita[16] has derived the equation,

$$\frac{d\varepsilon}{da} = -\frac{(\varepsilon-1)(\varepsilon+2)}{a} - \frac{8\pi}{E^2}\left(\frac{dA}{da}P_e^2 + \frac{dB}{da}P_eP_x + \frac{dC}{da}P_x^2\right)\frac{1}{2a^3}, \tag{5}$$

where P_x is dipole moment caused by the displacement of ion pairs, P_e is dipole moment caused by the distortion of a negative ion, and, A, B, C are parameters depending on the lattice constant. The decrease of the dielectric constants with increasing pressure is due more to the increase of the second term than the increase of the first one. Thus, it may be suggested that the increase of the pressure dependence of the dielectric constants in γ-irradiated crystals is ascribed to the quantity of the increase of the second term.

ACKNOWLEDGMENTS

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