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COLOR CENTERS IN SODIUM IODIDE*

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Introduction

In our laboratory, the investigations were performed on the pressure effects on the color centers in LiF, NaCl, KCl, KBr, KI and AgCl crystals synthesized by Kyropoulos' method[1, 2, 3]. Now, the author has synthesized NaI crystal and studied on the color centers produced by electrolysis and X-ray irradiation.

On the color centers in NaI crystal, Ottmer[4] reported about the easy bleaching of the F-centers in NaI produced by X-ray irradiation, but not the peak position. Mollwo[5] measured the peak position of the F-band at high temperature produced by additive coloring, and reported the extrapolated value, 588 mμ, as the peak position at room temperature. Ivey[6] reported the theoretical value, 606 mμ, as the peak position of the F-band.

The absorption bands of the color centers in NaI at room temperature were not yet studied in detail, so that the author has studied the heating effect on the shift of the absorption band of the color centers produced by electrolysis and the darknability of NaI by X-ray irradiation and has decided the peak position of the F-band.

Experimentals

The coloration of the crystal was performed by electrolysis and X-ray irradiation as follows.

Coloration by electrolysis The NaI specimens, 5×15×15 mm, were colored by electrolysis with a pointed cathode of nichrome and a flat anode of graphite in the furnace of 600°C and quenched into silicone-oil or in the air in order to investigate the quenching effect on the absorption bands of color centers produced by electrolysis.

For the purpose of observing the heating effect, the specimens,which were quenched in the air after electrolysis, were wrapped in tin-foil and reheated at 400°C, 500°C or 600°C for a definite time and rapidly quenched into CCl_4.

Coloration by X-ray irradiation The specimens of NaI, thalliated NaI and

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* *This investigation has been done by K. Shimizu, being in the postgraduate course, under the direction of Prof. R. Kiyama.*

1) S. Minomura, *This Journal*, **24**, 28 (1954)
2) R. Kiyama and K. Shimizu, *ibid.*, **25**, 41 (1955)
3) R. Kiyama and F. Okamoto, *ibid.*, **25**, 49 (1955)
4) R. Ottmer, *Z. Phys.*, **46**, 798 (1928)
5) E. Mollwo, *ibid.*, **85**, 56 (1933)
6) F. Ivey, *Phys. Rev.*, **72**, 341 (1947)

compressed NaI at 2,500 kg/cm for 24 hours in silicone-oil, were coated with silicone-oil, set in the dry box and irradiated directly with X rays (36kV, 15 mA) from the copper target with aluminum window for 10 minutes or 1 hour.

The absorption spectrum of these colored specimens was measured by means of Beckman model D U Quartz Spectrophotometer in the wavelength range from 400 mμ to 1,000 mμ. For the absorption measurement, the specimens were coated with silicone-oil and placed between the two glass plates for the protection from the humidity. The absorption bands of the glass, the silicone-oil and the X-ray irradiated silicone-oil were not observed in the wavelength range for measurement.

Results

Color centers produced by electrolysis

Quenching effect The NaI specimens were colored by electrolysis at 600°C. In the specimen immediately quenched into silicone-oil after electrolysis, the absorption band at 720 mμ and the weak band at about 600 mμ were observed (curve 1 in Fig. 1).

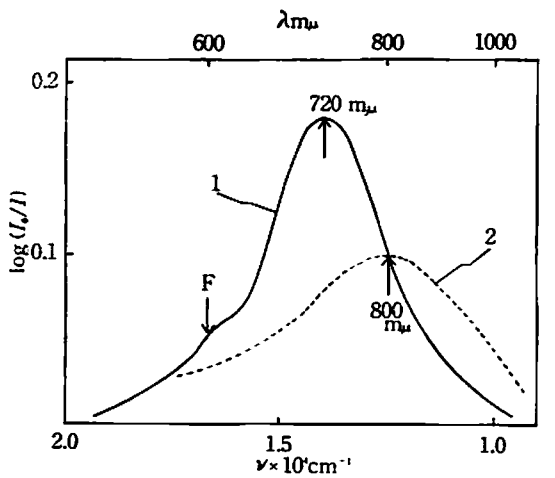

Fig. 1 Quenching effect on the absorption spectrum of color centers in NaI specimen produced by electrolysis at 600°C

1: absorption spectrum of specimen quenched into silicone-oil after electrolysis

2. quenched in the air after electrolysis

On the other hand, in the specimen quenched in the air after electrolysis, the specimen discolored with cooling and the Tyndal phenomenon was observed. The peak position of the absorption band in this specimen located at 800 mμ and the band height was lower than that of the specimen quenched into silicone-oil (curve 2).

Heating effect On the other hand, when the specimens quenched in the air after electrolysis were reheated above 500°C, the specimens colored blue. But, by reheating at 400°C, the specimens did not color.

By reheating at 600°C for 2 minutes and rapid quenching into CCl_4, the peak position of the absorption band shifted from 800 mμ (before reheating: curve 1 in Fig. 2) to the shorter wavelength side, 690 mμ and the band height increased (curve 2). At the same time, the weak band was observed at about 600 mμ. After further 2

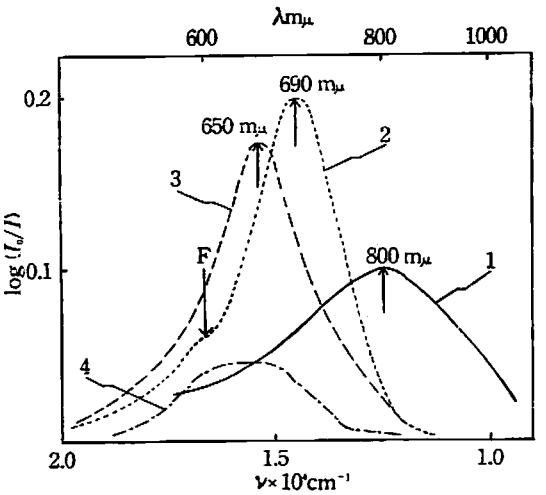

Fig. 2 Heating effect on the absorption spectrum of color centers in NaI specimen produced by quenching in the air after electrolysis at 600°C

1: absorption spectrum before heating
2: 2 minutes heating at 600°C
3: 3 minutes heating at 500°C
4: further 2 minutes heating at 500°C

minutes heating at 600°C, the absorption bands located at 690 mμ and at 600 mμ completely bleached and any other band could not be observed. In the case of reheating at 500°C for 3 minutes and rapid quenching into CCl_4, the peak position of the absorption band shifted from 800 mμ to the shorter wavelength side 650 mμ and the band height increased (curve 3). After further 2 minutes heating at 500°C, the band height decreased and the flat peak was observed (curve 4).

Color centers produced by X-ray irradiation

The absorption spectra in the specimens irradiated with X rays were shown in Fig. 3.

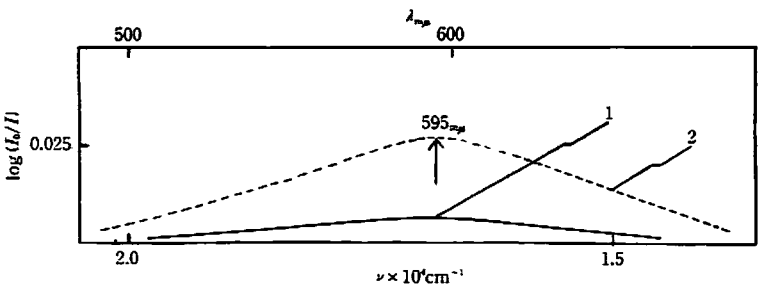

Fig. 3 Absorption spectra of the F-centers in NaI specimen produced by X-ray irradiation

1: 10 minutes irradiation
2: 1 hour irradiation

By irradiating the non-compressed NaI specimen for 10 minutes, a faint increase of the absorbance was observed (curve 1). After 1 hour irradiation, the absorbance increased and the peak position of the band located at 595 mμ (curve 2).

The thalliated NaI specimen was irradiated for 1 hour, but the specimen did not show the observable absorption band.

In the compressed NaI specimen at 2,500 kg/cm^2 for 24 hours, the absorption band produced by 10 minutes irradiation was almost identical with that of the non-compressed specimen.

Consideration

In the specimen rapidly quenched after electrolysis at 600°C, the weak absorption band was observed at about 600 mμ, and in the specimen irradiated with X rays, the absorption band was observed at 595 mμ. It is considered that these bands correspond to the F-band according to the extrapolated value, 588 mμ, given by Mollwo[5] and the theoretical value, 609 mμ, given by Ivey[6] as the peak position of the F-band.

The F-band produced by X-ray irradiation was faint, and the pressure effect could not be observed distinctly. These facts may be ascribed to the property of easy bleaching of the F-centers in NaI.

From the results that the absorption bands were produced in the long wavelength side of the F-band by electrolysis and that the peak position shifted to the longer wavelength side (from 720 mμ to 800 mμ) with the retardation of quenching and to the shorter wavelength side (from 800 mμ to 650 mμ) by reheating above 500°C, these bands are due to the colloidal particles[2, 7]. The colloidal band was observed more predominantly than the F-band. This fact may be attributed to the following reason: the F-centers in NaI produced by electrolysis easily coagulate so that the majority of the F-centers transform to the colloidal particles even in rapid quenching.

The author wishes to express his hearty thanks to Prof. R. Kiyama for his valuable guidance and encouragement during the course of this work.

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7) E. Mollwo, *Nachr. Akad. Wiss. Göttingen*, 254 (1932)