

THE AFTER-EFFECT OF HYDROSTATIC PRESSURE ON THE COLOR CENTERS IN NaCl*

BY RYO KIYAMA, SHIGERU MINOMURA and MASAHIRO ŌURA

Introduction

For the studies of the effects of hydrostatic pressure on the absorption bands in colored alkali halides, it has been published in the short report by Burstein, Oberly and Davisson¹⁾ that the band maxima of F-bands produced in alkali halides by X-ray irradiation shift to short wavelengths under hydrostatic pressure. Later, their shifts have been investigated in details by Jacobs.²⁾ It is mentioned in his private letter that the shift is restored to its original state after releasing the pressure.

The authors published at the same time as Jacobs did the effect of residual stress after the compression on the F-bands produced in alkali halides by an exposure to RaBr_2 , and found the shifts of band maxima of F-bands to short wavelengths, the decrease of spontaneous bleaching rate and the increase of darkenability.^{3, 4)} Afterwards, it has been experimented that the various band maxima produced in alkali halides by electrolysis at the temperature range of $550\sim 650^\circ\text{C}$ and in calcium fluoride by X-ray irradiation shift to short wavelengths by the residual stress.*

Now, the authors have investigated the effect of the residual stress and the temperature of electrolysis on the various absorption bands in NaCl produced by electrolysis at the temperature range $570\sim 790^\circ\text{C}$. Especially, it has been found that the absorption intensity of F-band increases and the intensity of the colloidal band of Na metal decreases with increasing temperature of electrolysis, and found that the shift of the band maxima of colloidal bands to short wavelengths with residual stress increases with increasing size of the colloidal particle.

Experimentals

Sample A large single crystal of NaCl synthesized from the commercial reagents made in Japan, having reagent proof, was used as the samples in this investigation. The specimens of the size of $4\text{mm}\times 10\text{mm}\times 13\text{mm}$ were cleaved from the same block of a single crystal.

* Part of this investigation was published by R. Kiyama, S. Minomura and M. Ōura in *Proc. Japan Acad.*, **30**, 764 (1954) (Communicated by S. Horiba, *M. J. A.*, Oct. 12, 1954)

1) E. Burstein, J. J. Oberly and J. W. Davisson, *Phys. Rev.*, **85**, 729 (1952)

2) I. S. Jacobs, *ibid.*, **93**, 993 (1954)

3) R. Kiyama and S. Minomura, *Proc. Japan Acad.*, **30**, 199 (1954)

4) S. Minomura, *This Journal*, **24**, 28 (1954)

Apparatus The high pressure apparatus for the compression of the specimens in mobil oil is the same as that in the previous papers.^{3,4)} The spectrophotometer for the measurement of the absorption band is the Beckman Model DU Spectrophotometer.

Procedure The coloration by electrolysis was conducted as follows: the specimens were set between a pointed cathode of platinum or nichrome and a flat anode of graphite (at the temperatures of electrolysis of 570~650°C) or of platinum (at the temperatures of 650~790°C), and heated at temperatures, 20°C apart over the range of 570~650°C or 40~50°C apart over the range of 650~790°C, and colored by applying the voltage of 50~500 volts (1~10 ma current) for a few minutes. The colored specimens were cooled at room temperature immediately after releasing the voltage, or cooled after preserving them at the temperatures of electrolysis for 10 and 80 minutes. The difference in the absorption bands by two methods of cooling was measured.

The central regions of the specimens were colored, but the outside regions completely colorless, and the samples, 1 mm thick, for spectral measurement, were cleaved from the central colored regions of the specimens. These samples were not colored homogeneously, but the position of band maxima located at the definite values throughout the entire samples. The optical density of the samples, $\log_{10}(I_0/I)$, where I_0 is the intensity of light transmitted through the virgin specimens and I is that of light transmitted through the colored specimens, were measured at a room temperature of 10~20°C. The samples were compressed in mobil oil at 7500 atm for 48 hours. After their compression in mobil oil, the samples were washed out with petroleum ether and wiped off with a piece of cloth. It was confirmed from spectral measurement that the mobil oil is excluded perfectly from the surfaces of the samples by these treatments.

NaCl colored by electrolysis were scarcely bleached at room temperature, but the samples were kept in the dark, except the time of sampling for compression and spectral measurement.

Results

The temperatures of electrolysis and the peak wavelengths of the absorption bands in NaCl before and after compression

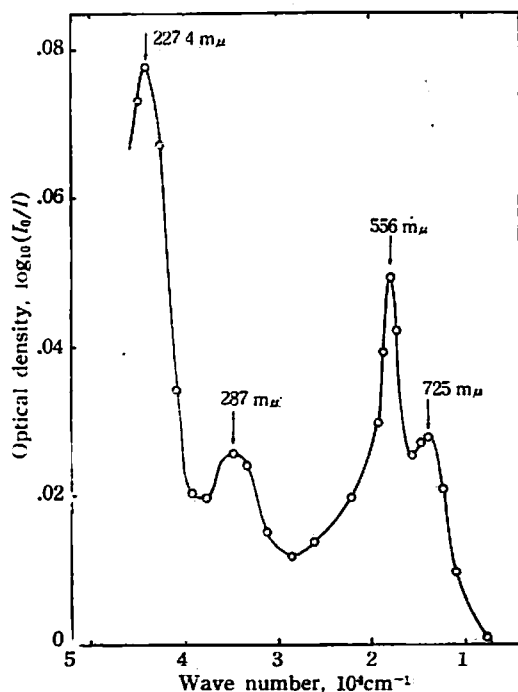


Fig. 1 The absorption bands by electrolysis at 570°C

are shown in Table.

The absorption bands in the sample cooled immediately after the electrolysis at a temperature of 570°C are shown in Fig. 1. The four absorption bands at $227.4\text{m}\mu$, $287\text{m}\mu$, $556\text{m}\mu$ and $725\text{m}\mu$ are found in this figure. These band maxima locate at longer wavelengths with increasing temperature of electrolysis (*cf.* Table, 1). The contours of absorption bands round $556\text{m}\mu$ varied with the temperatures of electrolysis above 650°C . It is shown in Fig. 2 that the absorption bands round $556\text{m}\mu$ in the samples cooled immediately after the electrolysis with platinum electrodes vary with the temperatures of electrolysis at $650\sim 790^{\circ}\text{C}$. At 650°C , the band at $620\text{m}\mu$ is observed (curve 1). At 700°C , the band at $461\text{m}\mu$ appears in addition to the band at $640\text{m}\mu$ corresponding to the band at $620\text{m}\mu$ mentioned above (curve 2). At 750°C , the intensity of the band at $472\text{m}\mu$ in the short-wavelength side grows larger than the intensity of the band at $670\text{m}\mu$ in the long-wavelength side (curve 3). At 790°C , the band at $477\text{m}\mu$ in the short-wavelength side is observed, but the band in the long-wavelength side disappears (curve 4). The two bands which varied in the same behavior as those in Fig. 2 are obtained by the electrolysis with the pointed cathode of nichrome.

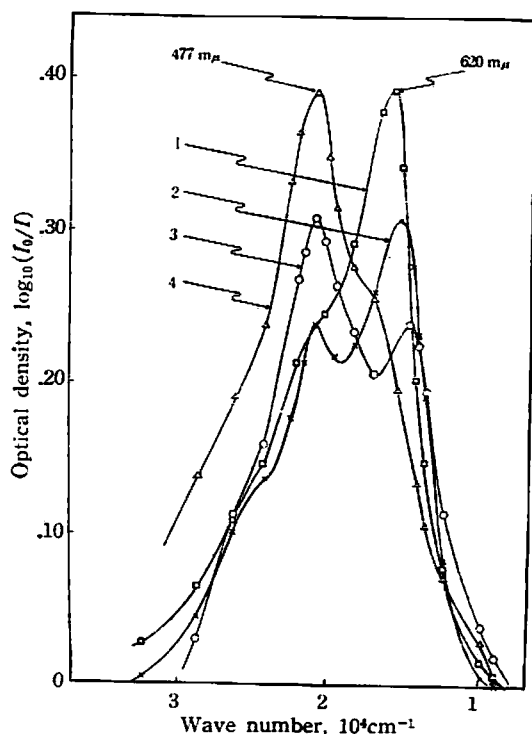


Fig. 2 The absorption bands by electrolysis at 650°C (curve 1), 700°C (curve 2), 750°C (curve 3) and 790°C (curve 4)

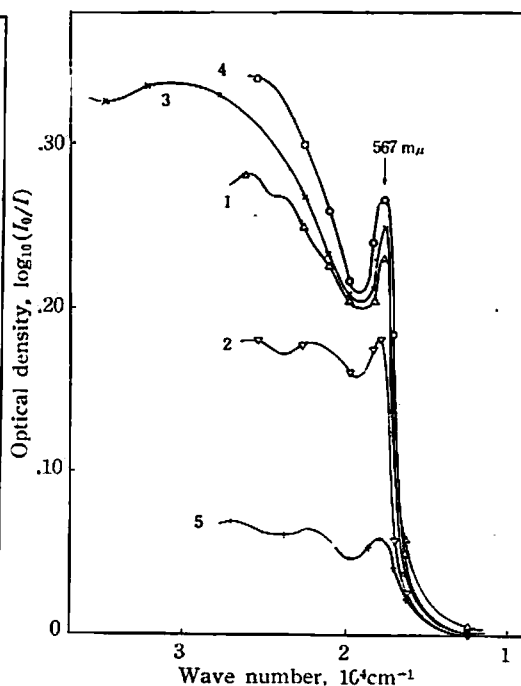


Fig. 3 The absorption bands with platinum electrodes preserved for 10 minutes at electrolysis temperatures of 650°C (curve 1), 700°C (curve 2), 750°C (curve 3) and 790°C (curve 4), and for 80 minutes at 650°C (curve 5)

The absorption bands in the samples cooled after preserving at 650~790°C for 10 or 80 minutes from the end of electrolysis with platinum electrodes are shown in Fig. 3 and differ remarkably from the bands in the samples cooled immediately after

Table The peak wavelengths of the absorption bands in NaCl by electrolysis before and after the compression

- 1) The bands in the samples cooled immediately after the electrolysis with a platinum pointed cathode and a graphite flat anode

Temperature of electrolysis °C	287 m μ -band		556 m μ -band (colloidal band)	
	Before the compression ± 0.2 m μ	After the compression ± 0.2 m μ	Before the compression m μ	After the compression m μ
570	287.0	286.0	556	555 (Fig. 1)
590	287.0	286.0	556	555
610	288.0	286.0	557	555
630	288.5	286.0	561	558
650	288.5	286.0	562	558

- 2) The bands in the samples cooled immediately after the electrolysis with platinum electrodes (Fig. 2)

Temperature of electrolysis °C	461 m μ -band (F-band)		620 m μ -bands (colloidal band)	
	Before the compression m μ	After the compression m μ	Before the compression m μ	After the compression m μ
650	x	x	620	605
700	461	457	640	620
750	472	465	670	645
790	477	470	x	x

- 3) The bands in the samples cooled immediately after the electrolysis with a nichrome pointed cathode and a platinum flat anode

Temperature of electrolysis °C	466 m μ -band (F-band)		568 m μ -band (colloidal band)	
	Before the compression m μ	After the compression m μ	Before the compression m μ	After the compression m μ
650	x	x	568	562
700	466	460	574	568
750	465	458	584	574
790	478	472	x	x

- 4) The bands in the samples cooled after preserving at the temperature of electrolysis for 10 minutes from the end of electrolysis with platinum electrodes (Fig. 3)

Temperature of electrolysis °C	566 m μ -band (colloidal band)	
	Before the compression m μ	After the compression m μ
650	566	563
700	565	561
750	567	563
790	567	560

the electrolysis in Fig. 2. The absorption bands corresponding to the bands at $620\sim 670\text{m}\mu$ in the long-wavelength side in Fig. 2 are found at $565\sim 567\text{m}\mu$ and huge absorption bands at the short-wavelength side. The two bands at 650°C shown in Fig. 3 were bleached out by preserving the sample at the same temperature for 80 minutes. The huge absorption bands in the short-wavelength side are not found in the samples electrolyzed with the pointed cathode of nichrome.

The positions of the band maxima shift to short wavelengths with the residual stress after the compression, and their shifts in wavelength increase for the band locating at longer wavelengths with increasing temperature of electrolysis.

Discussion

Scott⁵⁾ has investigated the relation between F-bands and colloidal bands produced in alkali halides by the additive coloration and found that the intensity of F-bands increases and the intensity of colloidal bands decreases with increasing temperature of coloration. Mollwo⁶⁾ has indicated that the absorption bands locating at $550\sim 650\text{m}\mu$ which are produced in the naturally or additively colored NaCl by quenching from the temperatures of $550\sim 650^\circ\text{C}$ and are stable at room temperature are colloidal bands of Na metal.

The relation between the bands in the long-wavelength side ($620\text{m}\mu$ -band in Table, 2) and the bands in the short-wavelength side ($461\text{m}\mu$ -band in Table, 2) shows the similar behavior with temperature to the relation between F-bands and colloidal bands found by Scott. Therefore, it may be decided that the bands in the long-wavelength side are colloidal bands and the bands in the short-wavelength side are F-bands. Because the two bands in Table, 3 show the similar behavior with the temperature of electrolysis to the above, the bands ($568\text{m}\mu$ -band) in the long-wavelength side may be decided to be the colloidal bands of Na metal and the bands ($466\text{m}\mu$ -band) in the short-wavelength side to be F-bands. The $556\text{m}\mu$ -band in Table, 1 and the $566\text{m}\mu$ -band in Table, 4 may be decided to be colloidal bands.

The model that an electron is trapped by a negative-ion vacancy is assumed for F-center. The fact that the maxima of F-bands locate at longer wavelengths with increasing temperature of electrolysis is attributed to that the expansion of the vacant lattice sites is frozen by quenching. The shifts of the band maxima to short wavelengths with the residual stress after the compression are due to the decrease of the potential well radius of vacancy.

The model of colloidal centers are yet unknown, but it has been reported that the band maxima of colloidal bands locate at the longer wavelength with increasing size of colloidal particles. The colloidal bands in the samples cooled immediately after the

5) A. B. Scott, *J. Phys. Chem.*, **57**, 757 (1953)

6) E. Mollwo, *Nachr. Acad. Wiss. Goettingen*, 1932, 254 (1932)

7) M. Savostianova, *Z. Phys.*, **64**, 262 (1930)

electrolysis with platinum electrodes (620m μ -band in Table, 2) locate at far longer wavelength, namely are due to larger size of colloidal particle, than the colloidal bands in the samples cooled after preserving for 10 minutes at the temperature of electrolysis (566m μ -band in Table, 4), or than those in the samples cooled immediately after the electrolysis with nichrome cathode and platinum anode (568m μ -band in Table, 3). The shifts in wavelength of the maxima of colloidal bands to short wavelengths with the residual stress after the compression increase with increasing size of colloidal particles. The huge absorption bands in the short-wavelength side in Fig. 3 would be caused by platinum, because their bands could be obtained by the electrolysis with platinum cathode, but not with nichrome cathode.

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*The Laboratory of Physical Chemistry,
Kyoto University*