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CHANGES OF ABSORPTION BANDS OF ALKALI-HALIDE CRYSTALS COLOURED IN SEVERAL CONDITIONS

BY

Hisao YAGI

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ABSTRACT

When the alkali-halide crystals were coloured in various conditions, two more new bands were found. The one exists between F-band and K-band, and its nature may be colloids. The other exists between U-band and K'-band, and its nature is quite similar to K-band.

1. Introduction

V-bands of coloured alkali-halide crystals consist of $V_1 \cdots V_7$-absorption bands as reported by H. Dorendorf (**1**), and on the other hand, in the same region, K- and K'-bands were found in our laboratory (**2**), but K-band appears remarkably in the crystals coloured by electrolysis. When we coloured the crystals in various conditions, two more new bands were found. The one is on the side of longer wavelength than K-band, and the other on the side of shorter wavelength than K'-band. They are called W-band and K_2-band respectively. Only the existence of K_2- and W-bands was reported by M. Hacskaylo (**3**). The nature of K_2-band is similar to that of K-band, while the nature of W-band is different from that of known bands.

2. Experimental procedures

The NaCl, KCl and KBr crystals used in these experiments were grown in our laboratory (**4**) by Kyropoulos' method. In order to subject crystals to electrolysis, they were mounted in a furnace in a manner as shown in Fig. 1. (This is called "pointed-electrode method".) A crystal was supported between two iron rods which served as a part of electrical circuit supplying the current for electrolysis. The one rod (A) is pointed sharply at its end and acts as cathode. The other (B) contacts the crystal with the carbon plate covered with platinum foil and acts as anode. All parts except the furnace can be evacuated. Current is supplied by a 450 volts power supply with a 500 KΩ resistor.

After inserting a crystal in the furnace, the temperature of the furnace was first raised up to 450°~500°C, and the current was supplied, and coloured cloud was made electrolytically in the crystal. (This coloured condition is called "F-coloured".)

Then, the temperature of the furnace was brought down to 350°~400°C, and the coloured cloud in the crystal was removed by reversing the polarity of the current. (This coloured condition is called "K-coloured".)

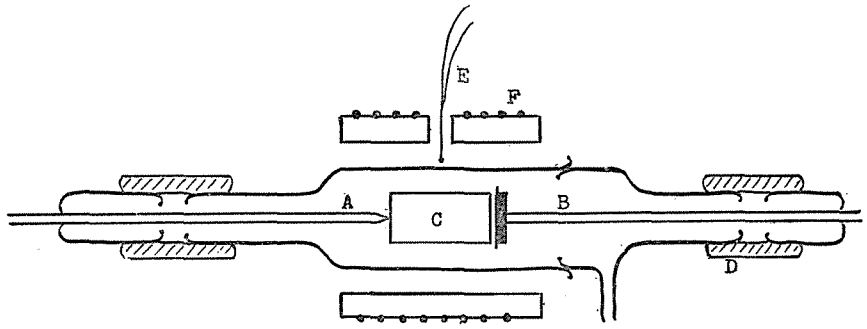

Fig. 1. Arrangement for subjecting crystals to electrolysis.
A: cathode, B: anode, C: crystal, D: rubber,
E: thermocouple, F: furnace.

For the irradiation with X-rays, a Mazda Sealex tube was used which was operated at a voltage of 30 KV D.C. and a current of 8 mA. During the irradiation, the temperature of the crystal was variable from 20°C to 300°C.

As a general rule, the crystals used were freshly cleaved on all sides at the last possible moment before starting an experiment.

The absorption spectra of the crystals were obtained with a Beckman Quartz Spectrophotometer Model DU which permitted measurements in the spectral range of 210~1000 mμ.

3. Results obtained

Generally speaking, in the case of X-ray coloured crystals, V_2-band appears remarkably and then appear K-, K′- and V_3-bands at room temperature. In the case of electrolytically coloured crystals, however, V-band does not appear (5)*, but U-, K-, K_2-, K′- and W-bands appear in respective conditions. The spectral location of the absorption bands in the region between F-band and U-band is shown in Table 1.

Table 1. The spectral location of the absorption bands.
(unit: mμ)

Bands / Crystals	U	V_3	V_2	K_2	K′	K	W	F
NaCl	192	210	222	230	258	293	328	465
KCl	215	215	232	345	267	307	348	560
KBr	230	232	265	280	290	320	375	631

* Recently V-band was also found by Y. Uchida and Y. Nakai by a special method.

A. *W-band*

When the crystals are electrolyzed in vacuum, W-band appears on the side of longer wavelength than K-band. W-band of NaCl crystal F-coloured at relatively lower temperature and then K-coloured at relatively higher temperature is shown in Fig. 3. When irradiated by the light lying in this band, this band did not change, but when irradiated by the light lying in K-band, only K-band was reduced. That is, W-band is not destroyed by the light lying in itself.

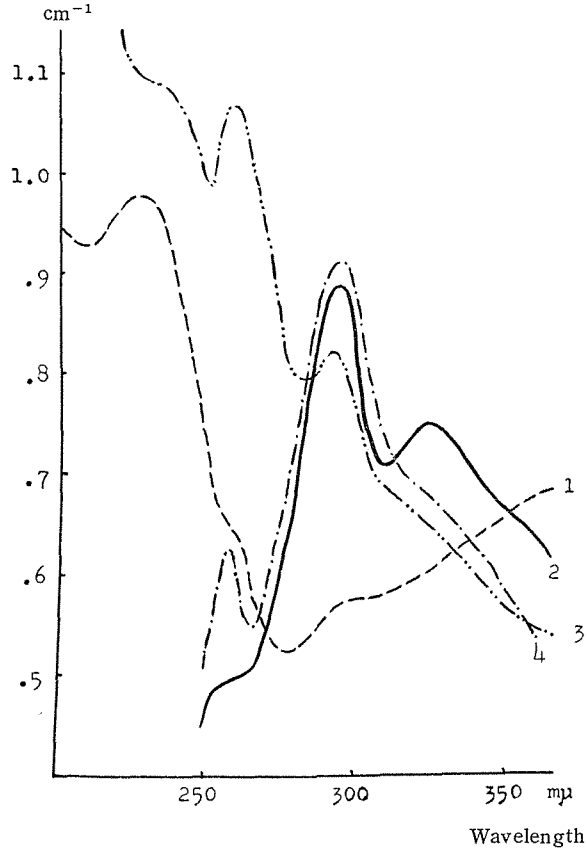

Fig. 2. Absorption bands of coloured NaCl
1. X-rayed
2. K-coloured in vacuum
3. F-coloured in vacuum
4. K-coloured in air

When brought up to 500°C, W-band became destroyed, separated with K-band and vanished at last. When the coloured NaCl crystal was brought up to 200°~250°C, R→K, K_2 and K′ transformation occurred, but in this case, W-band did not change.

The nature of W-band may be quite different from that of known bands in coloured alkali-halide crystals. So, we think, that is colloids of Na atoms.

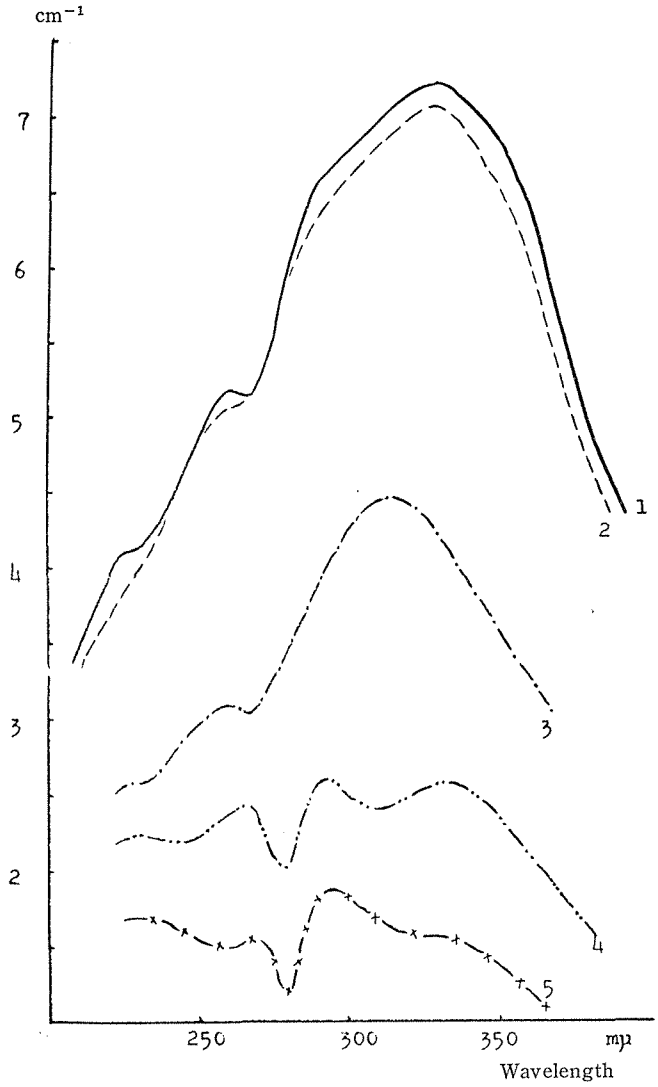

Fig. 3a. W-band of NaCl
1. K-coloured in vacuum
2. Exposed to K-light for 3.5 hours
3. Heated at 500°C for 3 hours
4. Heated at 550°C for 2 hours or more
5. Heated at 500°C for 2 hours or more

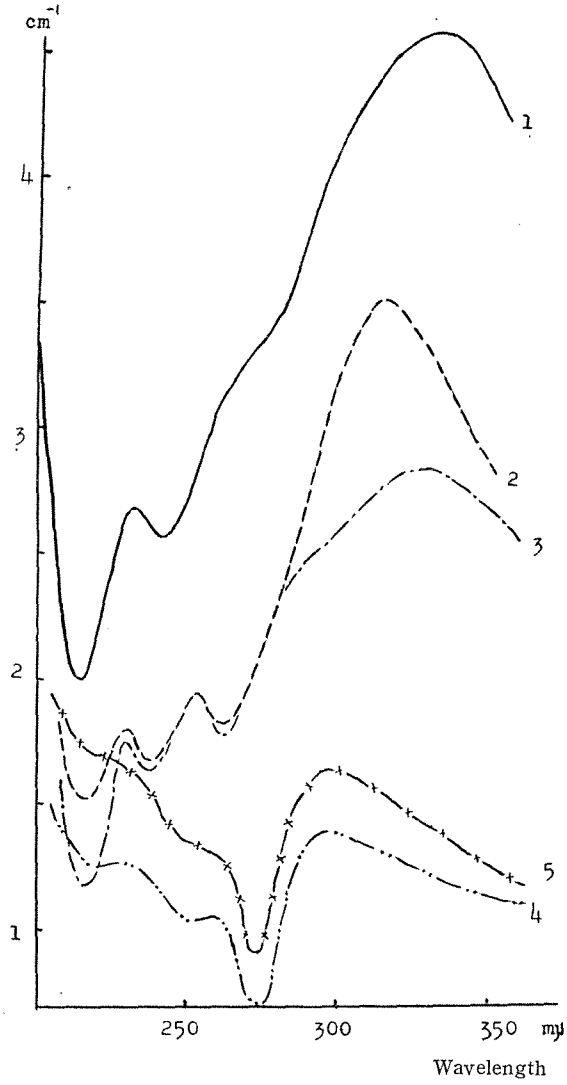

Fig. 3b. W-band of NaCl

1. K-coloured in vacuum
2. Heated at 500°C for 3 hours
3. Exposed to K-light for 1 hour
4. Heated at 500°C for 7 hours or more
5. Heated at 180°C for 4 hours or more

B. *K_2-band*

K_2-band appears in the crystals K-coloured at relatively low temperature or rapidly cooled after electrolysis. When brought up to 500°C, K- and K_2-bands were destroyed, and K_2-band was destroyed more easily than in the case of K-band. U-band on the

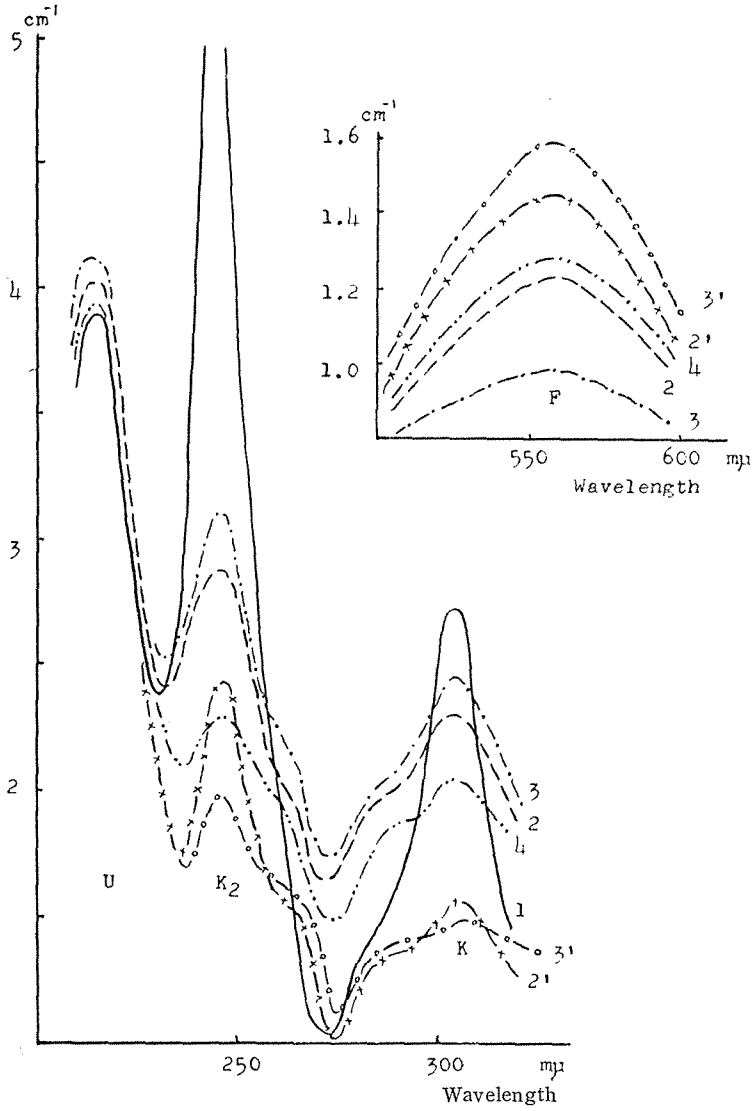

Fig. 4a. K_2-band of KCl
1. K-coloured in air
2. Bleached with K_2-light for 2.5 hours
3. Bleached with F-light for 2 hours or more
4. Bleached with K_2-light for 2 hours or more
2′. Bleached with K_2-light for 3 hours
3′. Bleached with K-light for 2 hours or more

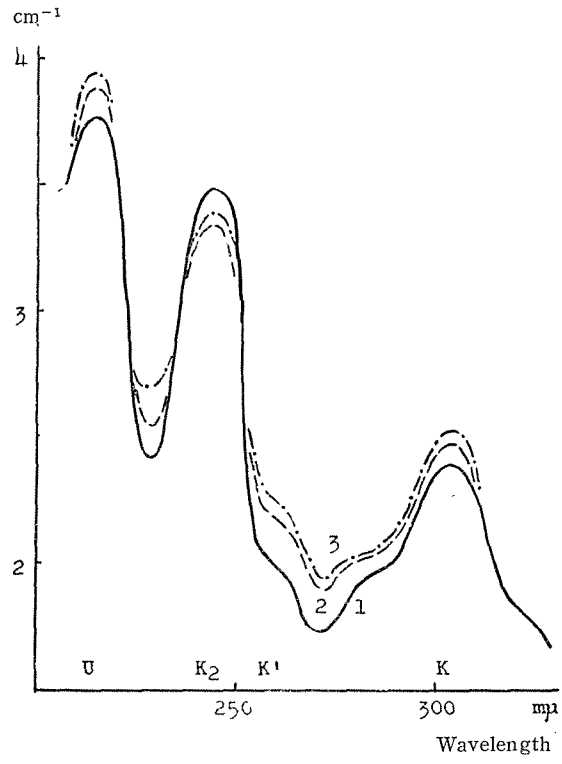

Fig. 4b. K_2-band of KCl
1. K-coloured in air
2. In the dark for a week
3. Bleached with R-light for 2.5 hours

side of shorter wavelength than K_2-band did not change. So this band is weak for the thermal treatment and so this band may not be found in past coloration.

By exposure to K_2-light or K-light, K-and K_2-bands were reduced and F-band was enhanced (Fig. 4-a). By exposure to F-light, F-band was reduced and K-, K_2- and K'-bands were enhanced. By exposure to R-light, K-, K_2- and K'-bands were enhanced. In these photo-transformations, the amount of transformation of K_2-band is larger than that of K-band.

When the coloured KCl crystal was brought up to 200°~230°C, R-band was destroyed and K-, K_2- and K'-bands were enhanced.

The nature of K_2-band is similar to K-band, except the weakness for thermal treatment.

C. *Crystals exposed to X-rays*

When the KCl crystals are exposed to X-ray, in the ultra-violet region, V-band

appears remarkably at room temperature. But when exposed to X-ray at high temperature (~ 300°C), W-, K-, K_2-, K′ and V-bands also appear as shown in Fig. 5.

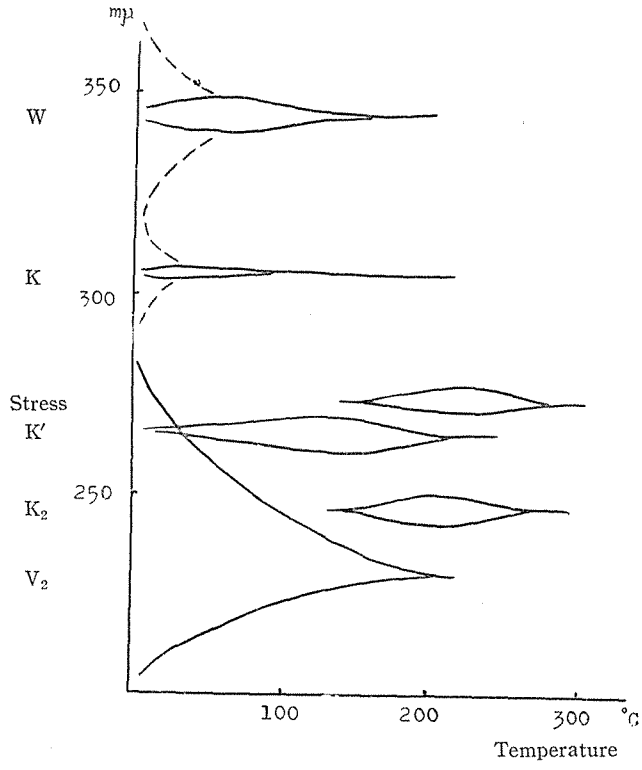

Fig. 5. Location of absorption bands of X-rayed KCl

D. *Stress-band*

When the KCl crystal was brought up to 500°C and rapidly cooled or subject to normal electrolysis for a short time, a new absorption band appeared in 275.5 mμ, and its absorption coefficient was about 0.2 cm^{-1}. When brought up to 500°C and subjected to electrolysis using iron string as anode and platinum plate as cathode, this band also appeared strongly and its absorption coefficient amounted to 1.5 cm^{-1}.

By exposure to the light lying in this band, this band did not change. When brought up to 500°C and slowly cooled, this band vanished, and this heat treatment is reversible.

This band also appears in the crystal exposed to X-ray heating up to 200°C.

The nature of this band may be in accordance with the stress growing in the crystal lattice. So this is called stress-band.

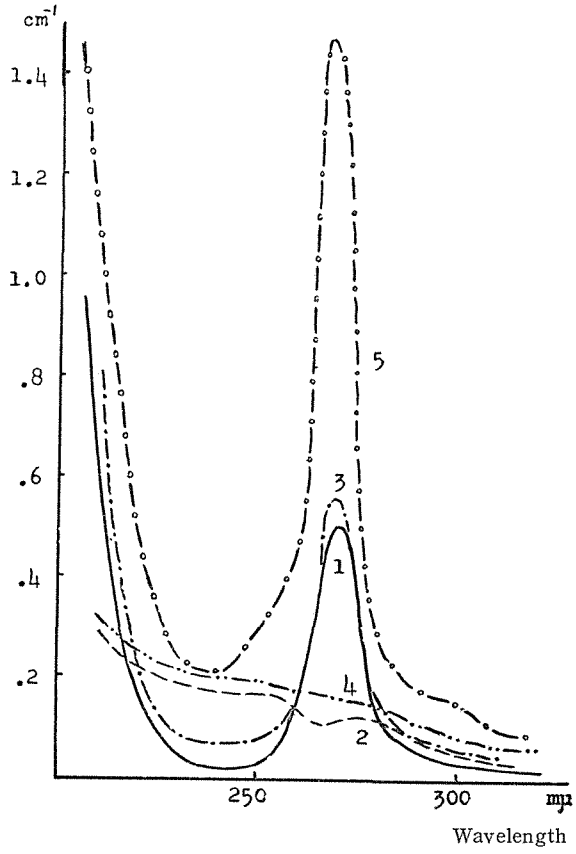

Fig. 6. 275.5 mμ stress band of KCl
1. Heated at 480°C for 2 hours and cooled rapidly
2. Heated at 500°C for 4 hours or more and cooled slowly
3. Heated at 500°C for 2 hours or more and cooled rapidly
4. Heated at 500°C for 2 hours or more and cooled slowly
5. Subjecting crystal to electrolysis and cooling rapidly

4. Discussion

When growing W-band, the crystal had to be slowly cooled in vacuum chamber after heating and its character was very different from other known bands. And so we wonder whether its nature can be colloids.

On the other hand, K_2-band is similar to K-band and its nature is the same one. But their energy states may be different on account of any element in the crystal. Hacskaylo mentioned in his paper that colour cloud in an electrolytically coloured crystal is removed either by reversing the polarity of the current or by continuing the flow of current in the same direction. These states are called metastable states.

Our K- and K_2-bands may appear in his metastable states. But, since these bands are different from stress-band, their nature may not be simple stress or deformation in crystal.

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