

SPECTRA OF COLOURED LITHIUM FLUORIDE CRYSTALS

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(Received March 1, 1956)

ABSTRACT

Absorption bands of coloured lithium fluoride crystals in the wavelength regions between 1600~5500 Å were measured. These correspond respectively to K, F, R, M and N bands which were found in the absorption spectra of coloured alkali-chloride and alkali-bromide crystals.

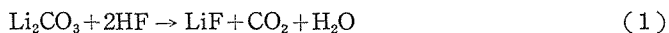
1. Introduction

The analogy between the absorption spectra produced in coloured alkali-chloride and alkali-bromide is fairly clear and so corresponding bands in each of them can be classified as U, V, K, F, R, M and N. In the case of lithium fluoride, correspondence has not been so clear, but recently interesting results have been obtained by C. J. Delbecq and P. Pringsheim (1). This may be due to following reasons: Pure natural LiF crystals have not been obtained, but recently synthetic optical LiF crystals were made. The fact that the first fundamental absorption band lies below 1200 Å renders the studying for bands of shorter wavelength side than F-band quite hopeless without the use of vacuum spectrophotometer.

Fortunately, in our laboratory we succeeded in making LiF crystals by Kyropoulos' method. So we studied the absorption spectra of coloured LiF crystals using quartz and fluoride spectrophotometers.

2. Experimental procedures

Although visible accomplishments had not been remarkable, Slater (2), Kyropoulos (3), Ramsperger and Melvin (4), and Gyulai (5) had been sufficiently encouraging to warrant a continuation of LiF crystallization studies on a smaller scale. But, Stockbarger (6) succeeded in that work. In our laboratory, Kyropoulos' method (7) was employed.



At first, LiF powders were made from pure Li_2CO_3 by chemical reaction (1) and then LiF crystals were grown from these LiF powders.

In order to subject the crystals to electrolysis, they were mounted in a furnace

in a manner as shown in Fig. 1. A crystal was supported between two iron rods which served as a part of the electrical circuit supplying the current for electrolysis. The one rod (A) is sharply pointed 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 volt power supply with a 500 K Ω resistor.

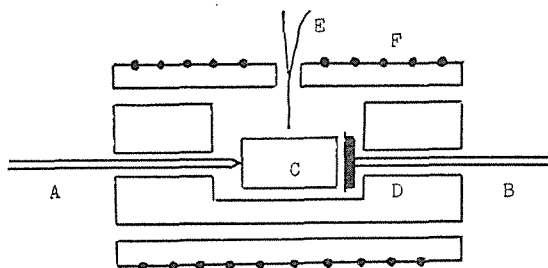


Fig. 1. Arrangement for subjecting crystals to electrolysis.

A: cathode,	D: holder,
B: anode,	E: thermocouple,
C: crystal,	F: furnace.

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 colour 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".)

For the irradiation with X-rays, a Mazda Sealex tube, operated at a voltage of 30KV D.C. and a current of 8mA, was used. During the irradiation the crystal was kept in dark and at room temperature.

The crystals used were always freshly cleaved on all sides at the last possible moment before starting experiment.

The absorption spectra of the crystals were obtained with a quartz-prism spectrophotometer with 1 meter focal length objective. Monochromatic light from the second slit was measured photoelectrically by Sb-photocell made of quartz and a Dolezalek quadrant electrometer (sensitivity: 1500 D/V) connected in the way as shown in Fig. 2. A CaF₂-prism vacuum spectrograph was used in the region between 2000 Å and 1500 Å and absorption spectra were obtained from the photographic plates by the recording microphotometer.

For the light source, a hydrogen discharge tube (6000 V, 1 A.) was used. RCA

photomultiplier tube 1P-28 was also used in place of the photocell. A Beckman Quartz Spectrophotometer Model DU was also used.

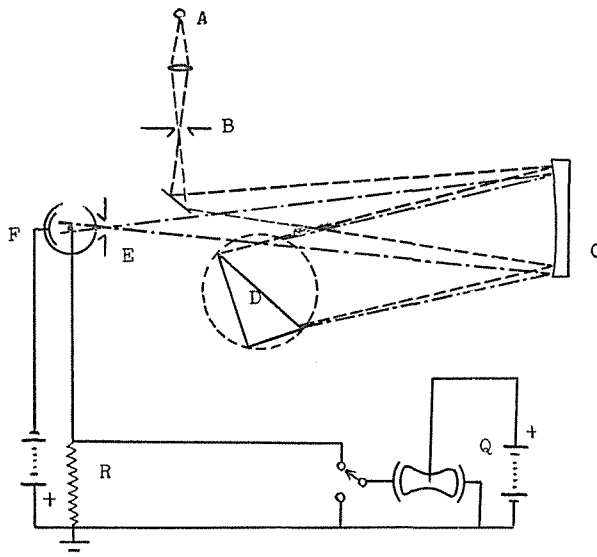


Fig. 2. Arrangement for measuring absorption.

- | | |
|-------------------------|----------------------------|
| A : light source, | E : 2nd slit, |
| B : 1st slit, | F : photocell, |
| C : collimator, mirror, | R : 10^{10} ohms, |
| D : prism, | Q : quadrant electrometer. |

3. Results obtained

Absorption spectra of coloured LiF-crystal is shown in Fig. 3, and wavelengths of their band maxima are given in Table 1. Values of these bands agree with those obtained from Ivey's empirical formula (8)* which has been derived from the values of absorption bands of NaCl, KCl and KBr. Among these R-bands, a peculiar wave number relation is seen as follows :

$$\frac{\nu_{\alpha} - \nu_{\beta}}{\nu_{\gamma} - \nu_{\delta}} = \frac{\nu_{\beta} - \nu_{\epsilon}}{\nu_{\delta} - \nu_{\zeta}} \quad \text{approximately.}$$

Our N-band corresponds to 520 $m\mu$ band found by Schneider (9) in LiF and near infra-red band in NaCl found by Molnar and in KCl and KBr by Oberly (10). Precise characters in N-band have not yet been known and only Petroff (11) reported that N-band appeared after M-band by exposure to F-light in KCl crystal.

* Ivey's empirical formula is given by

$$\lambda_{\max} = Cd^x,$$

where λ_{\max} is wavelength of absorption maximum of each band, d is the lattice constant of each crystal, C is a certain constant and x is a certain exponent. The latter two vary from band to band.

When K-coloured LiF crystal was irradiated by 546 m μ line of Hg lamp, N-band was reduced and F- and M-bands were enhanced as shown in Fig. 3. When this sample was measured while kept in dark room for two days, reduced band was

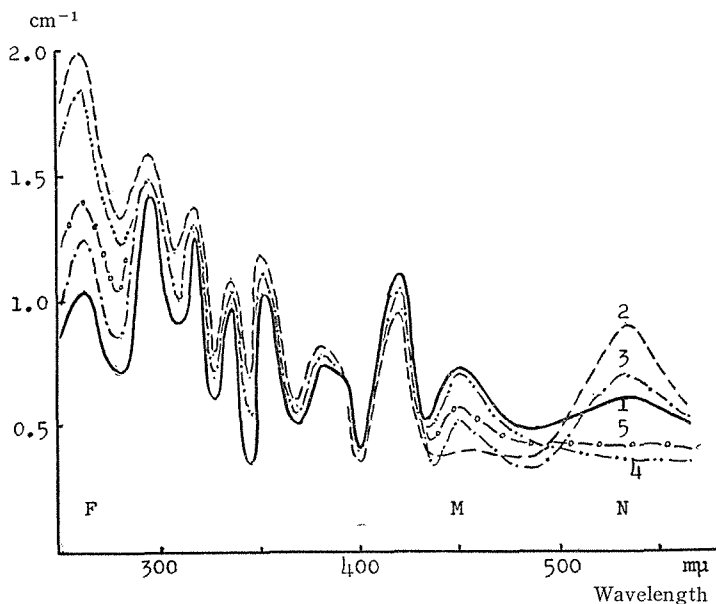


Fig. 3. Absorption bands of coloured LiF.

1. K-coloured
2. Bleached with Hg 465 m μ for 25 minutes
3. In the dark for 5 days
4. Bleached with Hg 546 m μ for 25 minutes
5. In the dark for 2 days

Table 1. Absorption bands of coloured LiF crystal.

Absorption bands	Wavelength in m μ	Energy in eV	Ivey's formula
N	530	2.33	1950 $d^{1.40}$
M	468	2.63	1780 $d^{1.36}$
R α	408	3.02	1330 $d^{1.55}$
R β	377	3.27	1260 $d^{1.54}$
R γ	355	3.47	1230 $d^{1.53}$
R δ	338	3.65	1170 $d^{1.54}$
R ϵ	315	3.91	1120 $d^{1.54}$
R ζ	297	4.15	1070 $d^{1.54}$
F	270	4.57	724 $d^{1.80}$
K	183	6.75	
K'	161	7.66	

These results were obtained at room temperature.

enhanced and enhanced bands were reduced and thermal equilibrium was accomplished. In this light bleaching, R-band did not change.

When irradiated by 435 m μ line of Hg lamp, M-band was reduced and F-, R- and N-bands were enhanced and the thermal equilibrium was obtained after three days. When M- and N-bands were bleached, relations of photo-transformation vs. time among various centres were shown in Tables 2 and 3. Numerical values in these tables are for $[(\kappa - \kappa_0)/\kappa_0] \times 100$, where κ_0 is the initial absorption coefficient and κ the absorption coefficient after bleaching.

Table 2. M-bleaching in LiF.

Bleaching time in minutes	Bands			
	F	R β	M	N
3	8	10	-20	90
5	6	7	-25	80
10	4	4	-28	60
20	2	1	-30	44
30	2	0	-32	44

Table 3. N-bleaching in LiF.

Bleaching time in minutes	Bands			
	F	R	M	N
3	5	0	20	-30
5	1	0	15	-40
10	-0.5	0	10	-50
20	-1	0	10	-55
30	-3	0	10	-60

When irradiated by the light of Hg lamp through Mazda UV-D1 filter (just lying in R-band) F- and M-bands were enhanced and N-band did not change.

By exposure to 185 m μ line of Hg lamp (just lying in K-band), F- and R-bands were enhanced as shown in Table 4.

Table 4. K-bleaching in LiF.
(unit: cm $^{-1}$)

Bands	F	R α	R β	R γ
Initial absorption	3.2440	1.9655	1.7620	2.2630
difference	+1.5	+0.5	+0.71	+1.9
Bleached for 5 hours	4.700	2.4305	2.4715	4.1050
difference	-0.3	-0.3	-0.3	-0.9
After 16 hours	4.4630	2.1450	2.1150	3.2220

Table 5. K'-bleaching in LiF.
(unit: cm $^{-1}$)

Band	F
Initial absorption	1.5940
difference	+0.96
Bleached for 5 hours	2.5540
difference	-0.06
After 16 hours	2.4145

By exposure to 165 m μ of H $_2$ discharge tube using vacuum spectrograph, F-band was enhanced as shown in Table 5.

Correspondence among the absorption spectra produced in coloured alkali-chloride, alkali-bromide and alkali-fluoride becomes fairly clear in these experiments. Precise investigation for each band has not yet been done, but it may be very interesting.

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