COLORATION OF THE ALKALI HALIDES BY X-RAYS

By P. L. Bayley

Abstract

Coloration of alkali halides and other salts by x-rays.—(1) *Hues produced.* CsF, RbF, CaF_2, CsCl, RbCl, KCl, NaCl, LiCl, AgCl, BaCl, BeCl, $CaCl_2$, CsBr, RbBr, KBr, KI, NaI, CdI, HgI and K_2SiO_3 were colored, whereas KF, NaF, LiF, NaBr, RbI, ZnCl, NH_4Cl and about 20 other salts showed no coloration with 5 hours exposure to intense radiation. (2) *Spectral absorption of colored halite and sylvite.* Halite (NaCl), colored amber, has a broad absorption band from 0.3μ to 1.3μ with a maximum at 0.46μ. Sylvite (KCl), colored purple, has a similar absorption band with a maximum at 0.55μ. (3) *Spectral fading of colored alkali chlorides.* The colors fade logarithmically when exposed to daylight, the time varying from a few seconds to days. When exposed to the spectrum of a 500 watt Mazda C lamp, colored NaCl, KCl, RbCl and CsCl fade most rapidly at wave-lengths 0.51μ, 0.61μ, 0.68μ and 0.62μ respectively. When correction is made for the energy distribution, halite and sylvite are found to fade most rapidly at wave-lengths where their absorption increase due to their coloration is a maximum.

HOLZKNECT[1] was the first to discover that x-rays produce in certain chemicals colors similar to those due to cathode ray bombardment and to exposure to radiation from radium compounds. Colors produced by any such type of radiation usually fade under the action of light. Holzknect found it necessary to cover many materials with black paper in order that the x-rays might produce coloration in them. For such substances, the rate of fading due to light in the room exceeded the rate of production of the color by the radiation. Attention was directed, in this laboratory, to these phenomena when Perrine,[2] studying the ultra-violet fluorescence produced by x-rays in such materials, noticed that in nearly every case the materials that gave off fluorescent light were colored at the end of the required long exposure. The author, after observing the hues[3] of the colors in many compounds, has studied the physical properties of the colors chiefly in halite (natural sodium chloride) and sylvite (natural potassium chloride).

A Coolidge x-ray tube of 30 m-amp. capacity was used and was operated at 50 kv and 3 m-amp. The samples were placed in a thin light-tight paper box within two inches of the tube and not more than

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[1] Holzknect, Verh. Deutsch. Phys. Ges. **4**, 25 (1902)

[2] Perrine, Phys. Rev. **22**, 48 (1923)

[3] Throughout this paper, colors will be described by the words *brilliance, hue,* and *saturation,* as defined in the Report of Committee on Colorimetry, J. Opt. Soc. Amer. R. S. I. **6**, 534 (1922)

five inches from the target. In all cases reported, where no color developed, the exposure was of five hours duration. The radiation was sufficiently strong to produce noticeable coloration in CsCl and KCl within five minutes. A fan was kept running to keep air circulating around the x-ray tube so that the samples would not get warm from the heat from the tube, since heating as well as exposing to light fades these colors.

STUDY OF HUES

The hue of the color produced depends upon the preparation of the sample. The coloration due to an impurity may mask that of the chemical under study,[4] and moisture of the sample may prevent coloration.[5] The more highly divided the particles of the material, the more unsaturated[6] are the colors. This is due to the large amount of white light reflected from the innumerable faces of the crystals of the powder. Although meaningless in general, the saturation of a few colors is given below in order to show a markedly higher saturation for those materials than for others of the same crystal size. In all the following work concerning the hues, the material was prepared in a fused mass or in as large crystals as possible so that coloration could be most surely detected if it existed.

In the table below are shown the hues observed for a group of halides. The results of a few other experimenters are included in order to show the variation in the colors obtained. The small letters after the hue indicate the speed of fading of the sample exposed to the daylight of an ordinarily light room; the capital letter refers to the experimenter, when other than the author and the final small letters to the methods of preparation of the samples, all as shown in the key following the table.

Since there seems to be no correlation between the color and the position of the element in the chemical table, no attempt has been made to state the exact hues. The word "bright" refers to the brilliance[3] and "deep" means highly saturated.

The chlorides of caesium, rubidium, and potassium were of such exceptional purity that the highly saturated colors produced in them if due to impurities must be due to extremely minute traces. Furthermore since the same hues are obtained in materials prepared by widely different methods, the coloration must be caused by the same impurities left in the compounds by several of the usual methods of purification.

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[4] Goldstein, Nature, **94,** 494 (1914)

[5] Goldstein, Ann. der Phys. **54,** 371 (1895)

[6] Doelter: (a) Das Radium und die Farben, Dresden (1910), contains references to all important papers of the subject up to the date of publication; (b) Sitz. d. K. Akad. Wiss. Wein. (I) **121,** 891 (1912); (c) Idem, (II) **119,** 1091 (1910)

The following materials also were found to be colored by x-rays: AgCl, permanent bluish gray; $BaCl_2+2H_2O$ and BaCl, pale yellow; BeCl, trace of yellowish brown; $CaCl_2$, pale yellow; CaF_2 natural crystal, purplish gray; CdI, permanent brown; HgCl, permanent brown; and K_2SiO_3 fused in flame, grayish blue.

TABLE I

Coloration of alkali halides by x-rays

For comparison coloration due to cathode rays is given in round brackets, and coloration by radium rays in square brackets

	Fluoride	Chloride	Bromide	Iodide
Cs	greenish blue, *bce*	deep blue, *f*, *abd* (no color—G) [greenish—D]	blue, *vf*, *ab*	
Rb	purple, *h*, *bce*	deep sky blue, *m*, *ad* (no color—G)	greenish blue, *vf*, *be*	no color, *be* (yellowish—G)
K	no color, *bce*	deep purple, *f*, *abd* violet, *f*—H (blue, *f*—N) (violet—G)	blue, *m*, *b* blue green, *m*—H) [sea green, *f*—N] (deep blue—G)	green, *m*, *b* [brown—N] (bright green—G)
Na	no color, *ac* (rose—G)	amber, *d*, *ab* chamois yellow, *m*—H [trace yellow—D] ([brown—N]) (amber, *m*—G)	no color, *a* (rose lilac—G)	brownish yellow, *d*, *b* (heliotrope, *m*—G)
Li	no color, *bce*	faint yellow, *h*, *b* straw, *d*, *c* (purple—G)	(dark gray—G)	(brown yellow—G)

Preparation of materials (When not otherwise stated, the material was only c.p. grade)

a: Open to atmospheric moisture.

b: Heated to about 200°C in a Pyrex tube; at that temperature the tube was sealed off with a flame some distance from the end of the tube so that moisture from the flame could not reach the sample.

c: Fused as a bead on a platinum wire in a bunsen flame; bead placed in a Pyrex tube and treated as in *b*.

d: Prepared by Dr. J. Papish of the Chemistry department, exceptionally pure; contained only spectroscopic traces of sodium, calcium, magnesium, iron, and silicon.

e: Prepared in Physics department by D. T. Wilber; made in paraffined paper dishes from c. p. halogen acid and alkali carbonate which was especially free from other alkalis.

Time of fading:

vf: Very fast, 1 minute or less.
f: 1 to 5 minutes.
m: 5 to 30 minutes.
h: 30 minutes to several hours.
d: one or more days.

Experimenter

D: Doelter[6]
G: Goldstein[7]
H: Holzknect[1]
N: Newberry and Lupton[8]

The following showed no coloration with 5 hours exposure: $AgNO_3$, $AgSO_4$, $CsCl_2I$, CsClBrI, $CsAl(SO_4)_2+12H_2O$, $Cs(NH_4)Cl$, $Ca(CH_3CO_2)_2$,

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[7] Loc. cit.[4,6a] and also many other references.

[8] Newberry and Lupton, Manchester Mem. **62**, (1918)

KCH_3CO_2, $KHCO_3$, KNO_3, KSO_4, K_2SiO_3 powdered, $LiCO_3$, $NaCO_3$, $NaNO_2$, Na_2MoO_4, $NaAlF_4$ (cryolite), $NaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, ZnCl.

SPECTRAL ABSORPTION OF HALITE AND SYLVITE COLORED BY X-RAYS

The sample of halite, which was quite clear, was a gift from the International Salt Co. of New York, Ithaca, N. Y., and came from the Detroit Rock Salt Co. A thin slab about 1 cm thick was cut out along natural cleavage planes. It was then ground down on very fine sandpaper until the thickness was uniform as tested by a micrometer caliper. The surfaces were polished by rubbing on chamois skin one half of which was barely moistened with water. While the sample was being rubbed back and forth on the moist portion, it was gradually drawn toward the dry portion, the rubbing being stopped just as the surface became dry. This process gave fairly polished surfaces.

The transmission was measured in the visible spectrum with a Schmidt and Hensch spectrophotometer. The transmission in the ultraviolet out to .200μ was measured by Miss S. A. McNulty with a Hilger sector disk spectrophotometer as modified by Howe,[9] and in the infra-red to 2.5μ by Prof. J. R. Collins.[10] The original sample showed a transmission of .87 at 2.5μ which decreased rather uniformly to .20 at 0.200μ. After coloration the sample showed absorption above that of the uncolored sample in the region between .3μ and 1.3μ. The curve plotted with ordinates equal to the ordinates of the transmission curve of the uncolored material minus those of the colored material will be referred to as the *color transmission* curve of the material. In the same terminology, then, the color absorption of halite begins at .3μ, has its maximum at .46μ, and ends at 1.3μ. The color absorption band is fairly pronounced, the ordinates of half the maximum occurring at .4μ and .5μ. The sample was left exposed to daylight during all of the following week and its transmission measured every day. The yellow color grew more faint but at every test the maximum absorption was found at .46μ.

Many samples of rocksalt from Detroit and Louisiana were colored and then heated quickly over a bunsen flame. The color faded rapidly but in no case did a blue color develop as has been reported for the case of coloration by cathode ray bombardment.[11] In a few samples a very pale pink color seemed to remain after the yellow vanished, but in every

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[9] H. E. Howe, Phys. Rev. **8**, 674 (1916)

[10] J. R. Collins, Phys. Rev. **20**, 486 (1922)

[11] Goldstein, Sitz. d. K. Akad. Wiss. Berlin 1894, p. 937.

case all color disappeared when the heating was continued to the point of the explosion of the crystal.

The sample of sylvite from Stassfurt was obtained from the Ward Natural Science Establishment. A plate about 2 mm thick was prepared in the same manner as that of halite. The sample faded so rapidly as a result of the light passing through it when its transmission was being measured, that in ten minutes all color had disappeared. The transmission was determined at intervals of .04μ from .47μ to .67μ. Settings of the Schmidt and Hensch instrument were made as rapidly and at as regular intervals as possible back and forth throughout the range. Thus a non-repeating set of curves was obtained showing less and less absorption, but each curve showed a maximum absorption at .55μ with half values at about .48μ and .63μ.

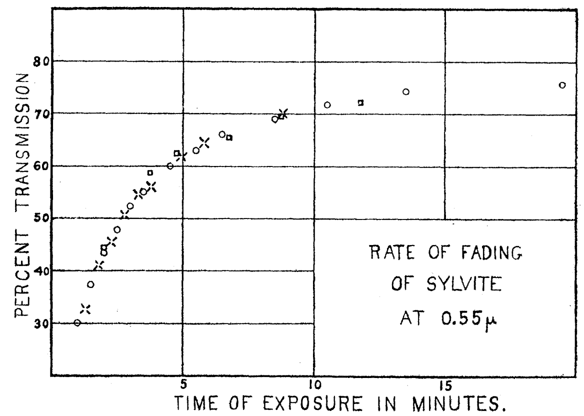

Fig. 1. Rate of fading of sylvite on exposure to daylight after coloration by x-rays.

Rate of Fading of Colors

The blue produced in caesium bromide by x-rays fades in less than 10 seconds exposure to daylight and is the shortest lived of any color observed by the author. The amber color of rocksalt is the longest lived. Sylvite fades rapidly enough to enable its rate of fading to be quickly determined. The same sample of sylvite used above was colored to .44 transmission. The spectrophotometer was set at .55μ, the position of maximum absorption. The adjustable slit was adjusted continuously to keep the fields matched in intensity and at regular intervals of time the slit width was recorded. The sample was again colored to .30 transmission, as it happened, and its rate of fading observed. A third test from .33 transmission was made. The data are shown in Figure 1. The curves have been shifted along the time axis to make the initial values of each curve coincide. It is seen that alternate coloration and fading do not change the optical transmission of the material. The curves vary slightly but not consistently. The rate of fading is approximately proportional to the existing saturation of the color, which suggests that the recombination involved is an ordinary photochemical reaction.

SPECTRAL FADING OF NACL, KCL, RBCL, AND CSCL

These four chlorides show highly saturated colors. They were each ground to a fine powder in a glass mortar and pressed in a very thin uniform layer on a glass plate. They were then moistened with a saturated solution of their respective salts and left to dry. Lithium chloride is too hygroscopic to be studied by this method. The materials formed a smooth surface sticking tightly to the plate, practically a thin sheet of very tightly packed crystals which had a minimum amount of reflected white light and so showed decided colors after exposure to x-rays. A plate of one of the colored salts was put in a plate holder and placed in a spectrograph. The image of a type C 500 watt mazda lamp with filaments in a plane was formed on the slit of the spectroscope. After a short exposure the plate holder was removed and the sample examined in a very dim light. The edges of the region of the material that was faded white were marked with a fine pencil and the material given a further exposure and the whole process repeated. Except for NaCl the edges of the faded region could be determined within 1 mm or .01μ. The total exposures were approximately 10 sec., 30 sec., 1 min., 5 min., and 10 min., but for NaCl the exposures made with wide slits were several hours and the edges of the faded regions were very indefinite. The results are shown in Fig. 2. The scales of the time ordinates have been changed for each curve to make them fit into the same space. After about 50 times the exposure necessary to produce the first noticeable fading, further exposures produced only extremely slow widening of the faded region.

The points of tangency of the curves with the wave-length axis gives the wave-length of most rapid fading. The maxima for NaCl and KCl are shifted toward the long wave-length side of the maximum absorption of halite and sylvite respectively. To show that the shift was caused by the larger amount of energy in the red end of the spectrum from the mazda lamp, the energy distribution from the lamp operated at 2850°C was calculated from Planck's radiation formula and corrections made for the absorption of the crown glass prism. A curve was plotted with the ordinates given by the product of the energy incident upon the sample and the percent color absorption of the sample. Those ordinates then represented the relative amounts of energy actually absorbed by the material and it was found that for halite and sylvite such curves had maxima respectively at 0.50μ and 0.595μ which are close to the wave-lengths of most rapid fading. The positions of the regions of most rapid fading are not all in the order of the atomic number of the alkali metals. That may be due to a peculiarity in the color absorption of RbCl and CsCl. Since large enough crystals of the latter two chlorides can not be obtained to make their color transmission determinable, it is hoped that their absorption can later be measured by the light which they reflect, although their rapid fading will make the work difficult. From the two cases completely studied it seems quite probable that the fading of materials colored by x-rays is primarily due to the energy gained by their color absorption alone.

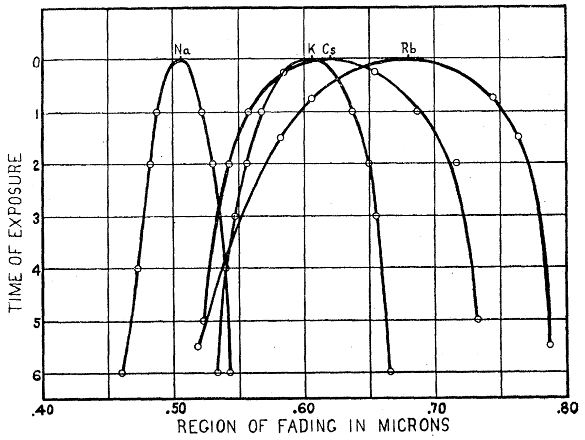

Fig. 2. Limits of faded region as a function of time of exposure in the spectrograph in arbitrary units.

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Cornell University.
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