

Optical Properties of Alkali Halides Containing Hydroxyl Ions*

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The optical absorption spectra of single crystals of sodium chloride, potassium chloride, and potassium bromide from various sources (Harshaw, Optovac, and NRL) have been measured from the visible region to the fundamental edge. Bands are found at 185 $m\mu$ in NaCl, at 204 $m\mu$ in KCl, and at 214 $m\mu$ in KBr. The positions of the bands satisfy an Ivey relation, $\lambda = 691d^{0.95}$, where d is the lattice parameter in angstroms. These bands are associated with the presence of hydroxyl ions in the lattice. When NaCl is additively colored, a hydride ion absorption (U band) appears which is proportional to the 185- $m\mu$ band absorption in the crystal before coloration. The F band produced in NaCl and KCl by ionizing radiation is also proportional to the initial hydroxyl ion band absorption. It is found that the hydroxyl ion absorption band can be removed by the addition of certain impurities to the melt.

I. INTRODUCTION

IT is well known that the optical and electrical properties of the alkali halides are affected by impurities.¹⁻³ Since the basic mechanism of color center production is not yet completely understood, an important step in determining the relative roles of impurities and mechanical strains would be to produce as pure crystals as is possible. Chemical analyses for trace impurities in the amounts often important in this field are tedious and not always fruitful, particularly when the impurity is unknown. The following are often used as general criteria of the "purity" of a crystal: (a) absence of optical absorption bands, (b) poor F -band production after exposure to ionizing radiation, (c) absence of optically excited fluorescence, (d) low extrinsic conductivity.

In the course of a previous investigation⁴ an absorption band was observed in NaCl at 185 $m\mu$. A similar, but hitherto unrelated, band has been found by many investigators⁵ in KCl at 204 $m\mu$. These bands are found in all synthetic NaCl and KCl crystals grown without the intentional addition of impurities. A specimen of rocksalt from Baden, Germany, shows virtually no 185- $m\mu$ band. Akpınar⁵ studied the effect of various additives and atmospheres on the band in KCl and concluded it was due to compounds containing oxygen.

Compton⁶ has recently suggested that hydroxyl ions in NaCl effectively sensitize the growth of colloidal particles by ionizing radiation. An enhancement in the F -band production by ionizing radiation has been observed by Smakula⁷ in crystals containing intentionally added impurities. There has apparently not been any

study made of such an effect in undoped crystals. A yellow fluorescence in the alkali halides has been observed by many investigators and has been studied most recently by Ewles and Barmby⁸ who attribute it to an O_2^+ center.

Applying the aforementioned general criteria for the "purity" it has been found that there are optical absorption bands, there is a strong dependence of F -band production on these bands, and that there is ultraviolet-excited fluorescence in all the synthetic crystals studied. No conductivity measurements were made. As a result of these investigations it is felt that the responsible impurity is the hydroxyl ion and accordingly the characteristic ultraviolet absorption band will be referred to as the "OH" band.

II. EXPERIMENTAL RESULTS

A. Crystal Growth

A study of the possible effects of the growth atmosphere, crucible materials, and impurities on the development of the 185 $m\mu$ and the 204 $m\mu$ bands in NaCl and KCl, respectively, was carried out. The most intensive investigation was on KCl in which the Kyropoulos technique was used for growing the single crystals. The growth was accomplished inside a capped quartz cylinder in which a slight positive pressure of the desired gas atmosphere was maintained. Single crystals obtained from Optovac were used as the starting material so that the initial optical properties could be measured and compared with those of the experimental crystals. The spectrum for the starting material is shown in Fig. 1(b). Identically shaped bands are observed at 204 $m\mu$ in crystals grown in atmospheres of dry nitrogen, dry argon, dry oxygen, or air. The band is considerably enhanced by growth in air while growth in the other atmospheres reduces it by a factor of two relative to the starting material. Argon was selected as the growth atmosphere for succeeding crystals unless otherwise noted.

* Presented by the authors at the American Physical Society meeting at Ithaca, New York, 19-21 June 1958. See Bull. Am. Phys. Soc. Ser. II, 4, 272 (1958).

¹ J. H. Schulman, J. Phys. Chem. 57, 749 (1953).

² F. Seitz, Revs. Modern Phys. 26, 7 (1954).

³ K. Przibram, *Irradiation Colours and Luminescence* (Pergamon Press, Ltd., London, 1956).

⁴ H. W. Etzel, Phys. Rev. 100, 1643 (1955).

⁵ For example: S. Akpınar, Ann. Physik 5, 429 (1940).

⁶ W. D. Compton, Phys. Rev. 107, 1271 (1957).

⁷ A. Smakula, Nachr. Akad. Wiss. Göttingen (1929), p. 110; Z. Physik 59, 603 (1930).

⁸ J. Ewles and D. S. Barmby, Proc. Phys. Soc. (London) 69, 670 (1956).

TABLE I. Crystal growth conditions and comparison of the 204- $m\mu$ band and the infrared data for KCl.

Crystal No.	Source	Crucible	Atmosphere	Additive	α_{204} (cm^{-1})	$^{16}\text{OH}^-$ (from infrared data)
...	Optovac	1.5	$<10^{16}$
19	NRL	gold	argon	none	0.7	$<10^{16}$
19'	NRL	gold	argon	KOH (0.1M%)	45-69	$1-2 \times 10^{17}$
20	NRL	platinum	argon	K_2CO_3 (0.1M%)	5-70	$1-2 \times 10^{17}$
21	NRL	platinum	CO_2	K_2CO_3 (0.1M%)	1.8	$<10^{16}$
22	NRL	platinum	O_2	none	1.8	$<10^{16}$
23	NRL	platinum	O_2	KOCN (0.1M%)	51-75	$1-2 \times 10^{17}$

Crystals were grown in crucibles of platinum, gold, and quartz. Crystallization from gold or platinum containers reduces the 204- $m\mu$ band by a factor of two. Crystals grown in quartz crucibles, however, show a reduction in the 204- $m\mu$ band of a factor of ten.

When 0.1 mole percent alkali hydroxide is added to the Kyropoulos melt, NaCl and KCl crystals show substantial increases in the 185- $m\mu$ and 204- $m\mu$ bands, respectively. For example, see Fig. 1(b). The same enhancement is obtained whether the crystals are grown in crucibles of gold or platinum. However, KCl crystals grown in quartz crucibles, even though doped with the same amount of alkali hydroxide, show less 204- $m\mu$ band than was in the Optovac starting material. Microscopic examination of the portion of the quartz crucible in contact with the melt indicates extensive pitting. When 0.1 mole percent K_2CO_3 is added to the melt, the single crystal grown in an argon atmosphere shows a factor of forty increase in the 204- $m\mu$ band whereas one grown in a CO_2 atmosphere shows a decrease by a factor of two in the band. The addition of 0.1 mole percent KOCN to the melt in a dry atmosphere also results in a factor of forty increase in the 204- $m\mu$ band.

B. Optical Absorption

Absorption spectra were measured from the visible region to 184 $m\mu$ by using a Cary Model 14M spectrophotometer. Measurements below this region were made with a Baird vacuum monochromator. Typical curves for the alkali halides investigated are shown in Fig. 1. It is found that the position of the 185- $m\mu$ and 204- $m\mu$ bands lead to an Ivey⁹ relation of the form $\lambda = 691d^{0.95}$, where d is the lattice parameter in angstroms. This predicts a band in KBr at 214 $m\mu$ which has been observed experimentally [Fig. 1(c)]. Measurement of these bands at 78°K indicates that they do not sharpen appreciably, and therefore are not as sensitive to changes in the lattice as are, for example, U and F centers.

Further association of the ultraviolet absorption bands with the hydroxyl ion concentration in the lattice is obtained from measurements of the infrared absorption due to the OH^- bond resonance. Table I indicates the relationship between the amplitude of the 204- $m\mu$

⁹ H. F. Ivey, Phys. Rev. **72**, 341 (1947).

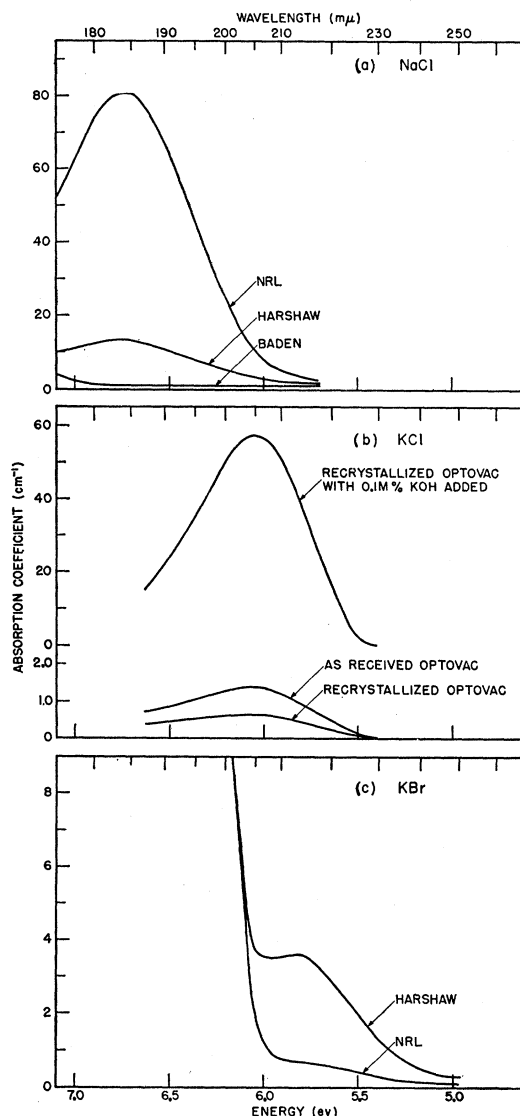


FIG. 1. The ultraviolet absorption spectra of NaCl, KCl, and KBr. Peak positions of the "OH" band are (a) 185 $m\mu$ in NaCl, (b) 204 $m\mu$ in KCl, and (c) 214 $m\mu$ in KBr. Crystals labeled NRL were grown in air. Harshaw and Baden crystals were measured as received. Recrystallized Optovac crystals were grown in dry argon atmospheres.

band and the number of OH^- centers calculated from the infrared resonance absorption in various KCl crystals. It can be seen that a measurable ($>10^{16}$ centers/ cm^3) OH^- resonance absorption is found only in those crystals which have a prominent 204- $m\mu$ band. The same correlation is found in NaCl with the 185- $m\mu$ band. The variation in the magnitude of the 204- $m\mu$ band in a given crystal reflects the hydroxyl ion concentration gradient in the crystal. The high absorption coefficient necessitates the use of relatively thin (about 0.4-mm) crystals in order to see the peak of the band. The hydroxyl ion concentration in these thin specimens varies according to their position in the crystal boule

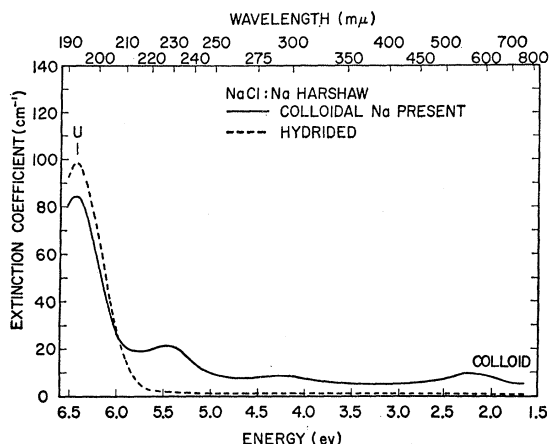


FIG. 2. Comparison of the absorption spectrum of a hydrided NaCl crystal with that of an additively colored (slowly cooled) NaCl crystal which contained a prominent "OH" band before coloration.

and so, accordingly, does their ultraviolet "OH" absorption. Similar variations were not observed in the infrared measurements since the absorption here is much weaker and hence much longer (about 20-mm) crystals are required to detect the band. Of the three crystals containing appreciable OH^- as determined by the infrared data, only one was doped with KOH. Despite reasonable precautions to exclude water vapor in the crystals grown with additions of K_2CO_3 and KOCN, the presence of an infrared OH^- absorption band was easily detected. The source of the hydroxyl ion in these crystals is unknown.

C. Coloration Properties

Additive coloration of NaCl crystals containing varying amounts of "OH" band produces three absorption bands in the ultraviolet at 192 $m\mu$, 228 $m\mu$, and 288 $m\mu$. These are shown in Fig. 2 together with a crystal containing a U band which is characteristic of the hydride ion absorption. Comparison (as shown in Table II) of the behavior of the U band with the 192- $m\mu$ band developed in the additively colored crystals indicates they are identical. The 192- $m\mu$ band produced by additive coloration of crystals containing the "OH" band is therefore ascribed to a hydride ion absorption. Figure 3 shows the dependence of the 192- $m\mu$ (U band) on the 185- $m\mu$ band in NaCl prior to additive coloration. Since all the crystals were colored simultaneously, this dependence indicates that the source of the hydride is the crystal itself rather than the excess sodium used in the coloration process. This conclusion is supported by the fact that the U band is also produced when a NaCl crystal is colored electrolytically. It should be pointed out that the same three ultraviolet bands appear in the electrolytically colored NaCl. Hacskeylo and Groetzinger¹⁰ have reported that the two bands of

¹⁰ M. Hacskeylo and G. Groetzinger, Phys. Rev. **87**, 789 (1952).

longer wavelength are present in their "precursor"-containing crystals. Limitations of their apparatus apparently prevented them from observing the U band. Their crystals show all the characteristics expected of a U -centered crystal.

Additive coloration of KCl containing various amounts of "OH" band does not yield as clear a picture of the production of U centers as was observed in NaCl. A well-defined U band is produced by additively coloring a crystal which has a relatively small "OH" band. Additive coloration of crystals with relatively large "OH" bands produces only a slight shift in the ultraviolet absorption to longer wavelengths. This is attributed to the growth of a U band which is apparently limited in KCl for some unknown reason. The dependence of the U band in KCl upon the "OH" band is therefore not as well established as it is in NaCl.

The F band produced by ionizing radiation is also found to be proportional to the preirradiation magnitude of the "OH" band in the crystal. In Fig. 4 is shown the F band produced in NaCl and KCl by soft x-rays. All crystals were cleaved to about 0.65 mm and irradiated under the same conditions (40 kvp, 16 ma, 5 minutes). With the growth of the F band there is found a decrease in the "OH" band and the simultaneous growth of a small subsidiary band on the long-wavelength side of the "OH" band. It is difficult to determine the exact position and shape of this subsidiary band because of its proximity to the decreasing "OH" band. However, its position suggests that it is the U band. An appreciable portion of the F centers produced can be ascribed to the loss in the "OH" band. The relationship between the two is evident from the fact that the growth of the F band and loss of the "OH" band cease simultaneously.

Previous investigators^{11,12} have studied the effects of Ca, Sr, and Cd on the production of F centers by ionizing radiation in NaCl and KCl. Colorability is greatly enhanced by the introduction of Ca and Sr. In the present investigation it has been found that the introduction of these divalent ions also removes the "OH" absorption band. It will be noted in Fig. 4 that the points scatter for KCl for small values of "OH"-band absorption. This may be attributed to the presence of a trace of Ca or Sr which decreases the "OH" absorption and increases the F band.

TABLE II. Comparison of 192- $m\mu$ band and U -band in NaCl.

Crystal	Peak position (ev)		Width at $\alpha/2$ (ev)		Peak shift $E_{77^\circ\text{K}} - E_{293^\circ\text{K}}$ (ev)
	293°K	77°K	293°K	77°K	
NaCl:NaH	6.51	6.59	0.72	0.53	0.08
NaCl:Na	6.50	6.57	0.74	0.50	0.07

¹¹ H. Hummel, thesis, Göttingen University, 1950 (unpublished).

¹² H. W. Etzel, Phys. Rev. **87**, 906 (1953).

It has also been found that the "OH" band can be removed by adding silica to the Kyropoulos melt, by premelting the Kyropoulos charge in HCl gas, or by baking a thin crystal at high temperature in HCl gas.

D. Fluorescence

A well-known yellow fluorescence is observed when many synthetic alkali halide crystals are excited with 253.7-m μ light. The fluorescence emission spectrum, consisting of nine maxima whose envelope peaks around 530 m μ , is quite similar in NaCl and KCl. These spectra have been reported most recently by Ewles and Barmby⁸ who have concluded they are due to O₂⁺. The dependence of the fluorescence on oxygen has been demonstrated in the present investigation by the growth of undoped crystals of NaCl in nitrogen, air, and oxygen and of KCl in argon and oxygen. A definite qualitative relationship between the oxygen concentration in the growth atmosphere and the fluorescence intensity was observed. No such correlation was found between the oxygen concentration and the "OH" band. This fluorescence seems to be associated with, but not directly due to, the "OH" absorption band. It is always found in crystals which have a substantial "OH" absorption. On the other hand, a crystal with substantial yellow fluorescence but no appreciable "OH" absorption can be produced by growth in a dry oxygen atmosphere. In addition, no fluorescence is excited by light absorbed in the "OH" absorption band. Maximum optical excitation of the yellow fluorescence occurs at about 260 m μ in NaCl and at about 270 m μ in KCl. The relationship between the "OH" band and the yellow fluorescence also holds in NaCl crystals doped with Ca and Cd. In the crystal containing Ca, both the "OH" band and the yellow emission are removed while neither is affected by the addition of Cd.

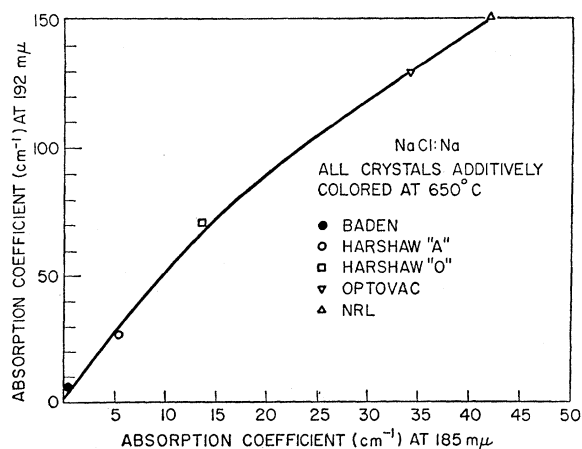


FIG. 3. Dependence of the *U*-band production upon the initial "OH" band absorption in additively colored NaCl. The crystals were slowly cooled from the additive coloration temperature. The designations Harshaw "A" and "O" denote different boules.

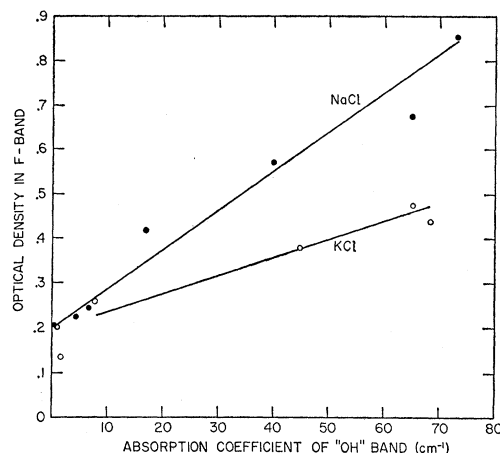


FIG. 4. The dependence of the *F* band produced in NaCl and KCl by ionizing radiation upon the initial "OH" band absorption.

III. DISCUSSION

It is felt that the preceding experimental results indicate that the ultraviolet "OH" absorption bands are due to hydroxyl ions in the crystal. Table I gives a comparison of the absorption coefficient for the 204-m μ band in KCl and the number of OH⁻ centers in the crystal determined from the infrared absorption at 2.7 μ . The ratio of the absorption at 204 m μ to the number of OH⁻ centers calculated from the infrared data is constant within a factor of two. Recognizing the limitations of Smakula's formula, an oscillator strength can be calculated for the ultraviolet "OH" band using the number of centers determined from the infrared data. The average value obtained is 1.9. Although a value less than one is expected for a one-electron center, this result is not considered unreasonable.

The optical properties of alkali halides are affected by the hydroxyl ion. The coloration produced by exposing such crystals to ionizing radiation is directly proportional to the "OH" band. It has been suggested by Seitz¹³ that the highly erratic values obtained for the efficiency of coloration at room temperature are due to chance impurities or the mechanical history of the specimens. More recently Gordon and Nowick,¹⁴ have suggested that the initial rate of *F*-center production by ionizing radiation is due to the presence of impurities. It appears, therefore, that a determination of the energy required to form an *F* center by ionizing radiation is likely to depend, at least in part, upon the amount of hydroxyl ion in the crystal investigated.

Additively colored crystals also appear to be influenced by the hydroxyl ion. Coloration, either by heating the crystal in an excess of alkali metal or by electrolysis and slowly cooling the crystal to room temperature, produces a *U* band¹⁵ in NaCl which is pro-

¹³ See reference 2, p. 63.

¹⁴ R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956).

¹⁵ H. W. Etzel, Bull. Am. Phys. Soc. Ser. II, **2**, 126 (1958).

portional to the "OH" band. Subsequent conversion of the U to the F band by ultraviolet irradiation yields an F band proportional to the initial "OH" band. The direct production of F centers in NaCl by quenching the crystal from the additive coloration temperature is possible, and yields the same dependence of F centers on "OH" centers but omits the interesting intermediate observation of the presence of U centers. The fact that U centers appeared when the crystals were slowly cooled first suggested that the 185- $m\mu$ band had hydrogen as a constituent. The intermediate U -center step is difficult to attain by additive coloration in KCl.

The absence of the "OH"-band absorption in NaCl crystals containing Ca and in KCl containing Sr suggests that the properties of these divalent doped crystals are in some way dependent upon the presence of hydroxyl ions. In contrast, however, the 185- $m\mu$ band in NaCl containing Cd is still present. Measurements of the OH^- resonance in the infrared in Ca doped crystals indicate that hydroxyl ions are present despite the absence of the 185- $m\mu$ band. The implication is that the 185- $m\mu$ center is destroyed by the divalent ion, perhaps with the formation of CaOH^+ or $\text{Ca}(\text{OH})_2$.

In 1940 Akpınar⁵ reported an extensive study of the 204- $m\mu$ band in KCl from which he concluded that the band was due to oxygen radicals in the crystals. One of his experiments included the doping of KCl with KOCN and growing a crystal in air and another similar one in nitrogen. The air-grown crystal showed a substantial 204- $m\mu$ band while the nitrogen-grown one did not. The explanation offered was that in the nitrogen case, the OCN^- radical had decomposed and that the partial pressure of oxygen over the melt in the air-grown case

prevented the decomposition and left the OCN^- radical in the lattice as such. In the present work, an attempt to reproduce the latter experiment under thoroughly dry conditions produced the same result, namely a substantial 204- $m\mu$ band. However, this crystal also showed the OH^- resonance band in the infrared, as have all the other crystals with substantial 204- $m\mu$ band absorptions.

The yellow fluorescence found in all crystals grown in air is undoubtedly due to the inclusion of oxygen during the growth process. The presence of the same fluorescence in hydroxyl-doped crystals grown in dry oxygen-free atmospheres must be due to some dissociation of the hydroxyl ion. The yellow fluorescence is not produced by the excitation of the hydroxyl ion since (a) it is found without the "OH" absorption in crystals grown in a dry oxygen atmosphere and (b) it cannot be produced by optical excitation into the "OH" band.

Author's note.—Since the completion of this manuscript a Letter by Rolfe¹⁶ bearing on the same subject matter has been published.

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¹⁶ J. Rolfe, Phys. Rev. Letters, 1, 56 (1958).