

## Effects of Oxygen and Water Vapor on the "OH" Absorption in Melt-Grown Alkali Halides

DAVID A. PATTERSON

*U. S. Naval Research Laboratory, Washington, D. C.*

(Received March 12, 1962)

Single crystals of KCl and NaCl have been grown from the melt with several changes in the ambient atmosphere during the growth of each crystal. The effects of atmospheres of water vapor and oxygen separately and combined on the ultraviolet "OH" absorption band have been examined. In KCl it was found that water vapor and oxygen are separately ineffective but together produce a continuously increasing "OH" absorption. In NaCl the increase is induced by water vapor alone. For KCl the rate of crystal growth in oxygen is found to be more than twice the rate in argon.

### INTRODUCTION

MANY nominally pure alkali halides glow with a yellow fluorescence when exposed to ultraviolet light. In KCl, KBr, and NaCl, this is due to absorption of the incident optical energy in a broad but very weak band around  $250\text{ m}\mu$  and its re-emission in a series of narrow bands whose envelope peaks around  $530\text{ m}\mu$ . These properties have been associated with oxygen in the crystal and the specific center involved has recently been identified as a substitutional  $\text{O}_2^-$  molecule-ion.<sup>1</sup> In this paper, the absorption will be called the oxygen or  $\text{O}_2^-$  band.

There is another absorption band at shorter wavelengths,<sup>2</sup> called the "OH" band, which is also found in many so-called pure alkali halides. This band is considerably stronger than the oxygen band but produces no fluorescent emission at room temperature. It has been connected with the presence of hydroxyl ions<sup>3</sup> in the crystal<sup>4,5</sup> although the specific configuration of the absorbing center has not yet been established.

The presence of the oxygen and hydroxyl impurities which cause these absorption bands also substantially alters many other physical properties of the crystals. Among the properties affected are; coloration by ionizing radiation,<sup>4,5</sup> ease and quality of cleavage<sup>5</sup>; thermal

conductivity<sup>6</sup>; mechanical relaxation<sup>7</sup>; and ionic conductivity.<sup>8</sup>

The oxygen fluorescence and its related ultraviolet absorption band can be considerably enhanced, without a corresponding increase in the "OH" band, simply by using an atmosphere of dry oxygen during crystal growth. On the other hand, a large increase in the "OH" band (e.g., by adding KOH to the melt) is always accompanied by a corresponding increase in the oxygen fluorescence.<sup>4</sup> Thus, there appears to be a one-way relationship between the "OH" and  $\text{O}_2^-$  band, in that the  $\text{O}_2^-$  band can be produced alone but the "OH" band cannot. This suggests that the production of hydroxyl centers is necessarily accompanied by the formation of  $\text{O}_2^-$  centers in the crystal. In the present work, the effects of atmospheric oxygen and water vapor on the "OH" absorption band in melt-grown KCl and NaCl crystals are examined.

### EXPERIMENTAL

A large single crystal of KCl from the Optovac Company was used as the starting material both to provide a common starting point of already purified material and to permit pregrowth optical measurements. This starting material was melted in a platinum crucible inside a closed cylindrical quartz growth chamber. A nonrotating, conduction-cooled platinum rod, entering through a small hole in the chamber lid, was used to initiate and pull the crystal from the melt. The growth atmosphere flowed continuously into the quartz cylinder throughout the entire process and escaped from it through the small access hole in the lid for the platinum rod. The gas was always passed through drying cells of Drierite and  $\text{P}_2\text{O}_5$ . Moisture was added, when desired, by bubbling the gas through a column of doubly distilled water 1 ft long just before introduction into the growth chamber.

In order to study the effects of the ambient atmosphere on crystals grown as nearly identically as possible, the atmosphere was changed several times during

<sup>1</sup> J. Rolfe, F. R. Lipsett, and W. J. King, *Phys. Rev.* **123**, 447 (1961).

<sup>2</sup>  $185\text{ m}\mu$  in NaCl;  $204.5\text{ m}\mu$  in KCl;  $214\text{ m}\mu$  in KBr.

<sup>3</sup> Some doubt of the connection between the "OH" band and hydroxyl ions in the crystal has been expressed. In NaCl in particular, carbonate has been suggested instead as the responsible impurity (reference 6). This possibility, in KCl at least, was discarded during the original work (reference 4) in the following manner. Four KCl crystals were grown in controlled atmospheres: (1) undoped in argon; (2) doped with KOH in argon; (3) doped with  $\text{K}_2\text{CO}_3$  in argon; and (4) doped with  $\text{K}_2\text{CO}_3$  in  $\text{CO}_2$ . Crystal (1) showed very little "OH" absorption and no infrared bands. Crystal (2) contained a large "OH" band, a clear infrared band at  $2.76\text{ }\mu$  due to  $\text{OH}^-$  resonance absorption, and no others. Crystals (3) and (4) both showed the infrared carbonate bands at  $11.35\text{ }\mu$  and  $7.10\text{ }\mu$ . In addition, crystal (3) showed both the ultraviolet "OH" band and the infrared  $\text{OH}^-$  band, while its  $\text{CO}_2$ -grown companion (4) showed neither. That is, (a) when either the ultraviolet "OH" band or the infrared  $\text{OH}^-$  resonance band appeared, the other was also found, and (b) the infrared  $\text{CO}_3^{2-}$  bands were produced both with and without the ultraviolet "OH" band.

<sup>4</sup> H. W. Etzel and D. A. Patterson, *Phys. Rev.* **112**, 1112 (1958).

<sup>5</sup> J. Rolfe, *Phys. Rev. Letters* **1**, 56 (1958).

<sup>6</sup> M. V. Klein, *Phys. Rev.* **122**, 1393 (1961).

<sup>7</sup> K. Brugger and W. P. Mason, *Phys. Rev. Letters* **7**, 270 (1961).

<sup>8</sup> F. Lüty (private communication).

the continuous growth of one long single crystal. Each change in atmosphere was "marked" on the crystal by a small change in diameter produced by briefly changing the crystal pulling rate. It was noted that the oxygen atmosphere had a marked effect on the rate of crystal growth. The growth rate of KCl in oxygen was more than twice the rate in argon.

The optical measurements were made with a Cary model 14M spectrophotometer. The crystal was cleaved lengthwise into three pieces and the center section was placed in the Cary sample chamber behind a stationary mask containing 1/16 in. wide slit. The crystal was then translated across the slit in small steps with a complete spectrum (350  $m\mu$  to 195  $m\mu$ ) run at each step. The usual base line and reflection corrections were made and the absorption coefficients calculated from these curves were plotted.

### RESULTS

The results for two single crystals of KCl are plotted in Figs. 1 and 2 as the absorption coefficient at 204.5  $m\mu$ , the peak of the "OH" band, vs the crystal length. In Fig. 2 the absorption coefficient (at 260  $m\mu$ ) in the  $O_2^-$  band has also been plotted. The vertical dashed lines indicate approximately where the changes in atmosphere were made and the atmospheres in which the respective sections were grown are as indicated. The times and approximate growth rates for each crystal section are also shown across the top of each figure.

The important effect of the atmosphere on the amplitude of the "OH" absorption band in the crystal is apparent in both figures. Since it is desired to examine the effects of moisture and oxygen separately and of them both together, the following discussion will proceed in that order.

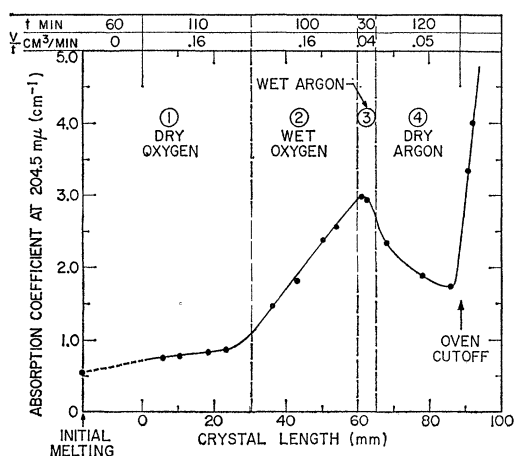


FIG. 1. The effects of different growth atmospheres on the "OH" absorption band in a single crystal of KCl. The absorption coefficient at the peak of the band at 204.5  $m\mu$  is plotted as a function of crystal length. The atmosphere changes are indicated by the vertical dashed lines. The times and approximate growth rates are shown at the top of the figure.

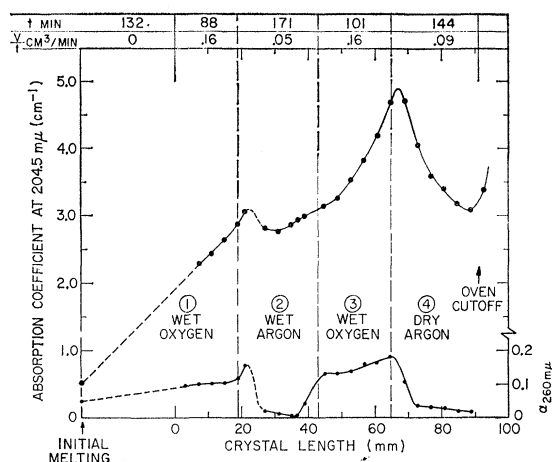


FIG. 2. The effects of different growth atmospheres on the "OH" absorption band in a single crystal of KCl. The upper curve shows the absorption coefficient at the peak of the band at 204.5  $m\mu$  as a function of crystal length. The lower curve shows the corresponding behavior of the  $O_2^-$  band measured at 260  $m\mu$  plotted on an expanded vertical scale. Atmosphere changes are indicated by the vertical dashed lines and times and approximate growth rates are shown across the top.

The effect of moisture alone has been observed in several KCl crystals (not shown) which were grown in very wet conditions.<sup>9</sup> These crystals showed only relatively small increases in the "OH" band (e.g., 0.6  $cm^{-1}$  in 5-h melt time) despite an initial excess and continuous supply of moisture. This same result is indicated in Sec. 2 of Fig. 2. Thus, moisture alone is very inefficient in producing the "OH" band in KCl.

An atmosphere of dry oxygen has little or no effect on the "OH" absorption in the crystal. An actual decrease has been reported<sup>4</sup> in one-stage crystals. In the present multistage crystal (Fig. 1 Sec. 1) the small increase is due possibly to incomplete drying of the gas or to diffusion of hydroxyl into the crystal during the growth of subsequent sections in wet atmospheres.<sup>10</sup> In any event, the increase is clearly small relative to that in the succeeding crystal section in which the major effect occurs.

The combination of oxygen and moisture in the growth atmosphere induces a relatively steep and continuous increase in the "OH" absorption in the KCl crystal. The increase caused by adding moisture to oxygen is seen in Fig. 1, Secs. 1 and 2. A similar increase resulting from the reverse procedure of adding oxygen to moisture is seen in Fig. 2, Secs. 2 and 3. Thus, oxygen and moisture together produce a continuously increasing "OH" absorption in the growing KCl crystal.

As a direct illustration that the atmospheric oxygen is going into the crystal, the absorption coefficient in the oxygen band has been plotted in Fig. 2. The similar be-

<sup>9</sup> The starting crystal was cleaved into thin plates which were stacked in the crucible with water drops between them and about  $\frac{1}{8}$  in. of water in the bottom. The growth was carried out in wet argon.

<sup>10</sup> W. D. Compton, Phys. Rev. **107**, 1271 (1957).

TABLE I. "OH" absorption coefficients in two crystals of NaCl.

Crystal section	Atmosphere	$\alpha(\text{cm}^{-1})$	Atmosphere	$\alpha(\text{cm}^{-1})$
1	Dry argon	1.4	Dry argon	2.6
2	Dry oxygen	2.7	Wet argon	15
3	Wet oxygen	21	Wet oxygen	20
4	Wet argon	29	Wet argon	41

havior of the "OH" and  $\text{O}_2^-$  bands and their dependence on the oxygen atmosphere can readily be seen.

The obvious dependence on time (i.e., crystal length) of the amplitude of the "OH" band in the crystal suggests that the hydroxyl impurity is going in, not directly from the atmosphere, but through an intermediate stage dependent on a reaction rate with the molten salt.<sup>11</sup> This conclusion is supported by the observation that the amplitude of the "OH" band measured in the starting crystal plots nicely onto the Sec. 1 curves when they are extrapolated back to the time of initial melting. This is true even in Fig. 2 in which initial melting was preceded by an 18-h flushing with wet oxygen to ensure atmospheric homogeneity. Thus, the "OH" band in the KCl crystal increases in proportion to the length of time the melt is exposed to wet oxygen.

When a KCl crystal is melted and regrown in a dry, inert atmosphere, its "OH" absorption is decreased. This decrease indicates that the hydroxyl ion would rather remain in the melt than go into the growing crystal (i.e., its distribution coefficient is less than one). This effect is apparent in the last sections of both figures. When wet oxygen is replaced by dry argon, the continuous supply of hydroxyl from the atmosphere is cut off and the hydroxyl-rich layer at the melt surface is depleted by inclusion in the crystal and by diffusion into the bulk of the melt. Hence, the decreasing local concentration and the normal rejection process combine to produce the rapid drop in the "OH" band in the growing crystal. The fact that the hydroxyl concentration in the melt is, in fact, quite high is demonstrated by the abrupt increase near the ends of the last sections in both figures. Both of these final sections grew unattended and were terminated automatically by a timer relay which cut off all power. This stopped the crystal elevator and allowed the oven to cool with the crystal in contact with the melt. The decreasing temperature caused the crystal to grow more rapidly, increasing the effective segregation coefficient toward unity and changing the hydroxyl concentration in the growing crystal toward that in the melt. The sharp increase in the "OH" absorption in the crystal which is seen to occur in the

vicinity of oven cutoff clearly demonstrates the higher concentration existing in the melt.

Two similar multistage crystals of NaCl were also grown from chemically pure salt which had been further purified by dithizone extraction of heavy metals. Unfortunately, neither was suitable for  $\alpha$  vs length measurements but some conclusions can be drawn from the "OH" absorption coefficients measured in each section which are listed in Table I.

As in KCl, dry oxygen has relatively little effect on the amount of "OH" absorption in the crystal. In contrast to KCl, however, it appears that moisture alone is now sufficient to introduce the "OH" absorption without the additional requirement of oxygen. This may have some bearing on the differences in structure between the oxygen fluorescence of NaCl and KCl at low temperature.<sup>1</sup>

The increase in "OH" absorption induced in a growing NaCl crystal by a moist atmosphere is ascribed to the simple hydrolysis reaction,  $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{HCl} \uparrow$ . Since KCl crystals grown in the same conditions do not show a similar increase in "OH" absorption, it is concluded that the hydrolysis reaction is inhibited in KCl for some reason, perhaps a higher solubility of HCl in the melt. The observed "catalytic" effect of the addition of oxygen may then be attributed to the removal of HCl by the reaction,  $2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 \uparrow$ . This conclusion is supported by the report<sup>11</sup> that passage of dry oxygen over molten NaCl produces free chlorine.

#### SUMMARY

Previous work has shown that the atmosphere in which an alkali halide crystal is grown from the melt can have a marked effect on its physical properties.

In the present paper it is found that:

- (1) Moisture alone has little effect on the amount of "OH" absorption in KCl but causes substantial increases in that band in NaCl.
- (2) Oxygen alone has little effect on the amount of "OH" absorption in KCl and NaCl. Oxygen does increase the rate of crystal growth of KCl to more than twice the rate in argon.
- (3) Oxygen and moisture together cause the "OH" band in KCl to increase in proportion to the length of time the melt is exposed to them. This increase is ascribed to a hydroxyl-rich surface layer on the melt created by a continuous reaction between the molten salt and the moist oxygen.
- (4) The hydrolysis reaction proceeds easily with molten NaCl but not with molten KCl unless oxygen is present.

<sup>11</sup> D. A. Otterson, J. Chem. Phys. **33**, 227 (1960).