

COLORATION OF ALKALI HALIDE CRYSTALS

by

Gerald Kirwin Ryan

A thesis presented to the Department of Chemistry of  
Union College in partial fulfillment of the requirements  
for the degree of Bachelor of Science in Chemistry.

By Gerald K. Ryan

Approved by Frederick F. Morehead

UNION COLLEGE  
LIBRARY

May 26, 1954

9  
UN92  
R988c  
1954  
c.2

## TABLE OF CONTENTS

	page
Introduction.....	2
History.....	4
Objective.....	6
Experimental Results.....	8
Analysis of Data.....	16
Bibliography.....	18

SEPT. 9, 1954

174431



## INTRODUCTION

Many crystalline solids, both naturally occurring as well as those artificially grown, display the phenomena of coloration and thermoluminescence as a result of the interaction of ionizing radiation with their lattices.

The phenomenon of coloration is very marked with simple alkali halide crystals. A crystal of potassium bromide, for example, when given an x-ray dose turns a distinct violet color. The intensity of this coloration depends upon the amount of irradiation absorbed. The color will gradually bleach when the crystal is exposed to light, particularly so when the incident light is of the same wavelength as that absorbed to produce the coloration.

Further coloration has been observed by other investigators in the range from ultra-violet through the visible.

A crystal which has been irradiated will, when heated, emit photons and simultaneously lose the coloration produced by the irradiation. This light emission is known as thermoluminescence and is often visible to the naked eye. The crystal, once heated and exhausted, will emit no further light until re-irradiated.

Other phenomena which accompany irradiation of these crystals are photoconductivity, decrease in density, fluorescence, and such effects which are related to the presence of electrons trapped in metastable levels near the conduction band. (2)



Coloration is known to be due to electrons trapped in lattice imperfections. These systems absorb photons which would ordinarily pass through the crystal, giving rise to absorption bands. Evidence seems to indicate that the color producing electrons are situated in missing anion sites in the crystal lattice. This color center is called a F-center. These vacancies move about inside the crystal lattice as ions move at finite temperatures, this being postulated by the laws of thermodynamics. When an alkali halide is exposed to x-rays or any ionizing radiation the electrons produced are trapped in these spaces left by missing anions. By absorbing a photon of the proper frequency or by acquiring energy from the thermal motion of the lattice, these electrons obtain enough energy to escape the trap and go into the conduction band. They may then be retrapped or fall to a ground state in a normally filled band. Sometimes a photon is emitted in this process. These processes are demonstrated in the coloring, bleaching, and thermoluminescence of an irradiated crystal.

The existence of F-centers in crystals is supported by experiments in which alkali halides were grown from a melt containing excess alkali metal. Crystals thus produced showed permanent coloration from color bands exactly like those produced by irradiation. In these experiments crystals were heated in the presence of the alkali metal or its vapors. The metal's electron goes to the site of the corresponding missing anion forming a F-center.



## HISTORY

The first observation of thermoluminescence is attributed to Boyle who reported it in 1663. Boyle discovered it accidentally while doing other work on diamond. During the next 250 years little work was done on this phenomenon and it was considered little more than a mineralogical curiosity.(3)

Geologists also recognized coloration and accompanying thermoluminescence in naturally occurring crystals but developed no adequate explanation of this phenomenon.

Charles Steinmetz did some work in the field of thermoluminescence of the alkali fluorides. He attributed its cause to the presence of rare earth impurities.

The first suggestion of the currently accepted theory of thermoluminescence was made by Meyers and Przibram who studied the luminescence and coloration produced in many artificial materials by high energy radiation. This theory was accepted by Lind and Bardwell as the explanation of the thermoluminescence and coloration of materials which had been exposed to radium. Lind and Bardwell have translated Meyers and Przibram from the original article as follows:

"certain groups of electrons are displaced by radiation from their normal positions and take up new metastable positions among the atoms." (4)

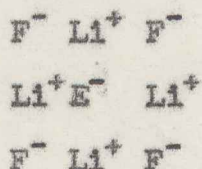
The coloration produced in these crystals by the radiation was attributed to the absorption of light by the displaced electrons. The loss of color and the thermoluminescence on heating was attributed to the return of the electrons to their normal position in the lattice.



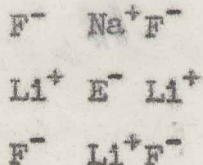
# OBJECTIVE

The original scope of this work was to study the coloration of lithium fluoride as a pure substance and lithium fluoride with impurities of sodium fluorid and lithium chloride. This particular salt was chosen because the study could be related to earlier work which had been done.

Because the main color bands were already known with some accuracy for lithium fluoride, it was thought to be interesting to find out what effect a foreign ion might have on the F-centers and the resulting coloration. It is known that a pure lithium fluoride crystal lattice having a F-center would appear like this:



and that the electron trapped in the center resonates among the six surrounding lithium ions. Thus, at a given time there is always one neutral lithium atom among the group. By adding a quantity of sodium fluoride impurity to the lithium fluoride a condition is bound to appear where a F-center is adjacent to a foreign sodium ion, as follows:



In this case the resonance would be disrupted, giving rise to new energy levels and the appearance of new color peaks. It was hoped that a quantatative relationship

between the intensity of these new peaks and the amount of impurities added might be found.

When lithium chloride is added as an impurity the anion is that which is foreign to the lattice. In this case, since the trapped electron does not resonate among the anions, a smaller effect on the coloration might be expected.

The color bands thus produced, or the light absorbance, were measured with a Beckman "DU" spectrophotometer.



## EXPERIMENTAL RESULTS

Since most alkali halides have a melting point between 600 and 1000 degrees Centigrade, their crystals are generally made by slowly cooling the desired molten salt. A platinum crucible is filled with the desired salt and heated in an electric furnace. The temperature is raised above the melting point and held there a short while. Then the molten mass is colled back to the melting point. The material is held at the melting point for a period of from several hours to one day. At this time it is allowed to slowly cool back to room temperature at a rate of about two degrees per hour. Care must be practiced in cooling the crystal since too rapid cooling causes sharp faults in the crystal lattice.

Voltage fluctuations of up to ten volts occur in the laboratory A. C. source. This amount of flutuation will cause a temperature fluctuation of fifteen degrees or more at higher temperature. This situation made the uniform cooling of the melt impossible until a constant voltage regulator was insertes in the circuit.

The crystal making appabatatus we employed consisted of an electric furnace operated in series with an A. C. ammeter and a 'variac' variable voltage output. Current was supplied by a 110 vo't A. C. source fed through a constant voltage regulator. Temperature was measured with a bimetallic thermocouple.



The furnace used in earlier crystal making attempts was a "Cenco" 345 watt, pot type, with nichrome resistance wire imbedded in its refractory cement sides. A special lid was constructed for this furnace since the standard one had no aperture through which the melt could be viewed. This was a necessary measure since the thermocouple could give only a close approximation of the temperature while the melt had to be maintained exactly at the melting point. This lid was made of refractory cement imbedding a wire mesh and bolted to a steel frame. It had a two cm. mica window and a smaller hole to accommodate the thermocouple lead.

The furnace described above worked well at temperatures up to 700 degrees C. but above this temperature the resistance wire in the walls became brittle and fractured. The furnace failed at sustained high temperatures.

For later work a Fisher '12660A' furnace was used which held up at temperatures in excess of 1000 degrees.

Twenty grams of lithium chloride was heated in a platinum evaporating dish to a temperature of 690 degrees on the thermocouple. At this point the salt melted completely. The temperature was then lowered to 642 degrees when the salt grew less transparent and a small crystal appeared on the bottom. The melt was allowed to remain at this temperature overnight and on the following day gradual cooling was begun. This cooling process lasted two days, until room temperature was reached. The salt had resolved itself into two transparent, nearly



flawless crystals, weighing about ten grams apiece.

Unfortunately, lithium chloride is so hygroscopic that it could not be handled in the manner our experiment required. The salt alone dissolves itself in moisture taken from the air. The crystals were almost immediately fogged over and all attempts to dessicate them failed. Immediately protecting the newly polished faces with transparent tape proved a failure since the tape did not transmit ultra violet in the spectrophotometer.

Due to the above, and because of the high melting point of lithium fluoride, work with the lithium fluoride series had to be abandoned for a more tractable salt. Potassium chloride with impurities of potassium bromide and sodium chloride was next chosen.

Crystals of pure potassium chloride were prepared successfully by slowly cooling the molten salt. Smaller crystals were split from the larger ones by cleaving along the planes of the lattice with a razor blade.

After the original crystal, attempts were made to grow ones with two, five, ten, twenty, and fifty mole per cent sodium chloride in potassium chloride. It was found that, regardless of the care taken in controlling temperature, the melts containing up to ten per cent impurity had only, in the crystalline part, 3.8 per cent sodium chloride.

The amount of impurity was determined by running a volumetric chloride analysis on a sample and from this result calculating the percent sodium ion. In each case,



the crystal mass, on cooling, formed a ring the center of which irregular, semi-crystalline appearing granules which were assumed to be sodium chloride which was not taken up into the crystalline area.

The melt containing 50 mole per cent sodium chloride and 50 mole per cent potassium chloride, on cooling, produced a homogeneous mass which was milk white with a glazed appearance. This mass afforded no crystals large enough to be examined on the spectrophotometer.

Twenty mole per cent sodium chloride in eighty mole per cent potassium chloride produced a homogeneous batch of crystals which were too small to be useful.

A crystal from the five mole per cent sodium chloride batch was subjected to an x-ray dose of 36,000 roentgens along with a crystal of pure potassium chloride. The x-rays were provided by the machine belonging to the Biology department on this campus. The impure crystal was analysed and found to contain 3.8 per cent sodium chloride. It had a thickness of 0.407 cm. The pure potassium chloride crystal was 0.1276 cm. thick. After irradiation both crystals took on a deep violet color. They were shielded from light to prevent bleaching and analysed in the Beckman spectrophotometer for light absorption.

The use of the spectrophotometer introduced an unavoidable error in this determination since the mono-



chromatic light used to analyse the crystal at the same time bleaches it to a certain extent. This error can only be partially avoided by the rapid reading of the machine while taking crystal absorption data.

Absorption data for the two crystals are shown in table I. This table tabulates optical density, which is equal to  $\frac{1}{L} \log \frac{I_0}{I}$ , where  $L$  is the thickness of the crystal, and the corresponding wavelength of the analysing light.

Special aluminum blocks were used to mount the crystals while analysing them in the photometer. These blocks were drilled with a hole about 0.5 cm. in diameter across which the crystal was pasted. These blocks were designed to fit into the cuvette holder of the photometer.

The curves describing absorption versus wavelength for this pair are in graph I. The abscissa is calibrated in wavelengths of light ( $\mu$ ) and the ordinates are units of optical density.

TABLE I

Wavelength (mμ)	Optical Density	
	KCl + NaCl	pure KCl
320	.270	.508
330	.300	
340	.351	.705
350	.371	
360	.371	.627
370	.359	
380	.357	.587
390	.360	
400	.360	.625
420	.378	
440	.405	.710
460	.452	
480	.535	.782
500	.708	
520	.970	1.010
540	1.152	1.252
560	1.230	1.620
580	1.142	1.395
600	.958	1.100
620	.868	.940
640	.651	.852
660	.517	.690
700	.342	.685



# GRAPH I

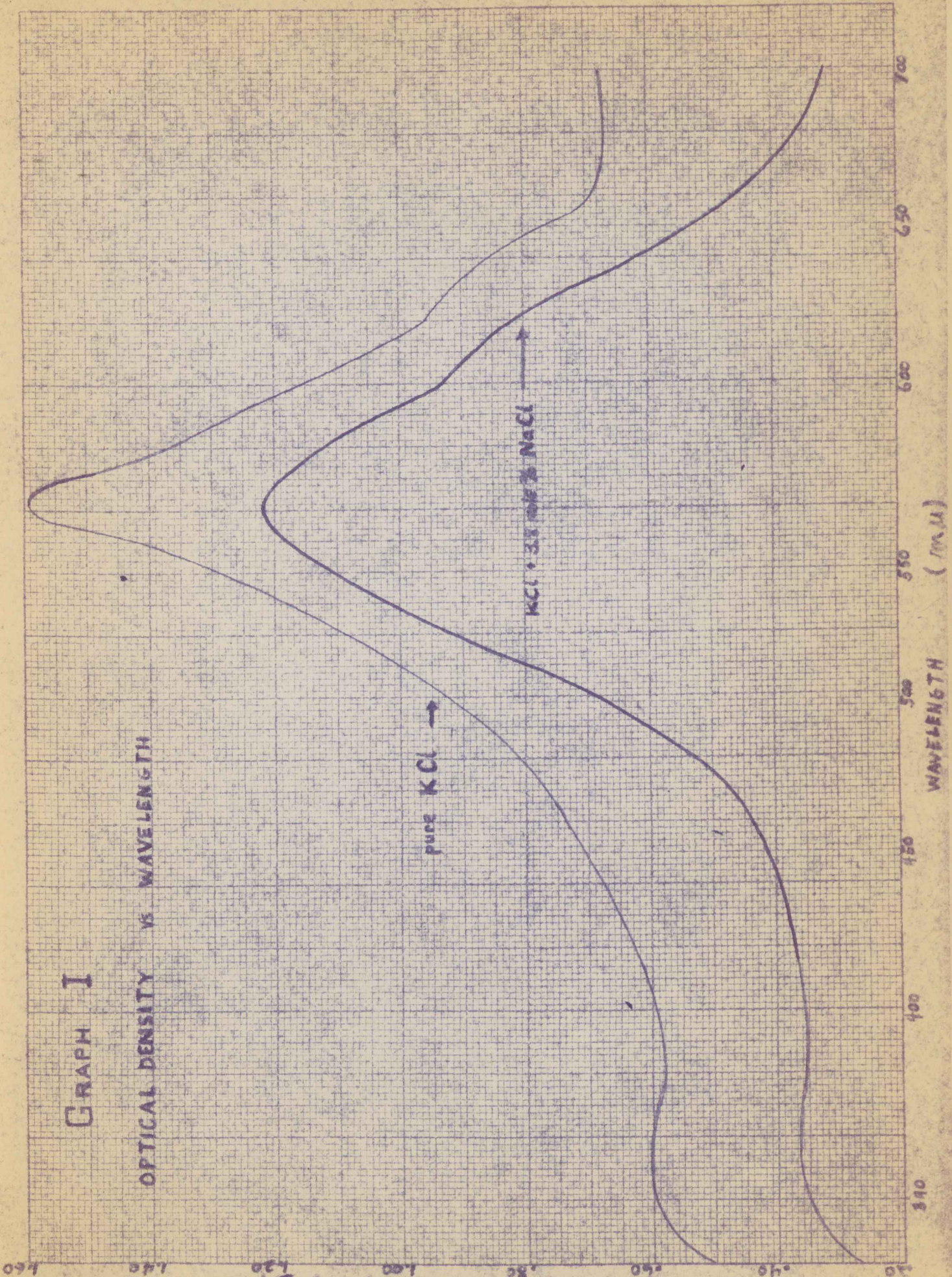
OPTICAL DENSITY VS WAVELENGTH

Optical Density ( $\pm \log \frac{I}{I_0}$ )

pure KCl →

KCl + 3.8 mm NaCl →

WAVELENGTH (mμ)





## ANALYSIS OF DATA

Comparing the optical density curves of pure potassium chloride to mixed potassium chloride and sodium chloride shows no new absorption peaks introduced by the sodium chloride impurity. Both crystals show maximum optical density at 560 mu. Furthermore, upon subtracting the absorbance of the unirradiated crystals from the absorbance of the irradiated crystals, and comparing the increase in optical density for several wavelengths of the pure and impure crystals, no difference was found. Hence, one can conclude that there is very little, if any, effect of impurities on intensity of coloration.

Failure of the crystals to show the expected effect of new absorption peaks from impurities might be laid to any one of three causes:

- 1) Lack of intense enough irradiation.
- 2) Not enough sodium ion introduced as impurity.
- 3) There is no effect.

The largest single dose of radiation we were able to obtain from the biology department was 36,000 roentgens. This dose was the result of one half hour exposure to their x-ray source. The effect of this exposure is shown in graph I, but on other occasions crystals exposed to only 12,000 roentgens did not exhibit absorption in the ultra violet at all but in the visible only.



It is possible that the crystals might show the expected absorption if they were exposed to much higher intensity irradiation such as that provided by a  $\text{Co}^{60}$  source or a high intensity betatron.

The second consideration, that there might not be enough impurity present to register an effect, could conceivably be corrected by purchasing ready made crystals which are sold by the Harshaw Chemical Co. Whether crystals, containing more than the optimum value of 3.8 per cent sodium chloride which we were able to produce, can be purchased is unknown. Perhaps with a more delicately, thermostatically controlled temperature regulating set-up a crystal containing more impurity yet of usable size could be grown.

BIBLIOGRAPHY

1. Morehead, F. F.; The Effect of Different Types of Radiation on the Coloration and Thermoluminescence of Lithium Fluoride; Ph. D. Thesis, Wisconsin, 1953
2. Daniels and Saunders; The Thermoluminescence of Crystals; Wisconsin, 1951
3. ibid
4. ibid
5. Seitz, F., et al; Imperfections in Nearly Perfect Crystals; Wiley and Sons, 1952