AD-783 328

GROWTH AND HARDENING OF ALKALI HALIDES FOR USE IN INFRARED LASER WINDOWS

William A. Sibley, et al

Oklahoma State University

Prepared for:

Air Force Cambridge Research Laboratory
Advanced Research Projects Agency

20 April 1974

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

ARPA Order No. 2055

Program Code No. 2D10

Contractor:
Oklahoma State University

Effective Date of Contract:
1 May 1972

Contract No. F19628-72-C-0306

Principal Investigator & Phone No.:
Dr. William A. Sibley
(405) 372-6211, Ext. 7525

AFCRL Project Scientist & Phone No.:
Major Normatas Klausutis
(617) 861-4841

Contract Expiration Date:
30 April 1975

Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to the National Technical Information Service.

Unclassified
Security Classification

AD-783328

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Oklahoma State University
Department of Physics
Stillwater, Oklahoma 74074

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP
N/A

3. REPORT TITLE
GROWTH AND HARDENING OF ALKALI HALIDES FOR USE IN INFRARED LASER WINDOWS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Scientific Interim.

5. AUTHOR(S) (First name, middle initial, last name)
William A. Sibley John R. Hopkins
Charles T. Butler Joel J. Martin

6. REPORT DATE
30 April 1974

7a. TOTAL NO. OF PAGES
31

7b. NO. OF REFS
34

8a. CONTRACT OR GRANT NO.
F19628-72-C-0306 ARPA ORDER No. 2055

9a. ORIGINATOR'S REPORT NUMBER(S)
Annual Technical Report No. 2

b. PROJECT, TASK, AND WORK UNIT NO.
2055 N/A N/A

c. DOD ELEMENT
61101D

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
AFCRL-TR-74-0220

d. DOD SUBELEMENT N/A

10. DISTRIBUTION STATEMENT
A. Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES
This research was supported by the Defense Advanced Research Projects Agency.

12. SPONSORING MILITARY ACTIVITY
Air Force Cambridge Research
Laboratories (LQ)
L. G. Hanscom Field
Bedford, Massachusetts 01730

13. ABSTRACT

Several KCl crystals have been pulled from melts of reagent grade KCl, RAP treated reagent grade KCl, and HCl/Cl_2 treated KCl. The OH^- concentrations and the 10.6μm optical absorption of these crystals were evaluated. The results indicate that both the RAP and HCl/Cl_2 treatments effectively remove OH^- and lower the 10.6μm absorption. However, for pulled crystals the rate of decrease of the 10.6μm absorption is less than that of the OH^- concentration as the duration of the RAP treatment increases. Radiation damage has been investigated as a supplementary mechanism for strengthening KCl-KBr alloys and polycrystalline KCl. The results show that the hardening due to the radiation damage is independent of the other mechanisms present. Hence, the total strength equals the radiation damage in the pure crystal plus the strength caused by either alloying or small grains. For an F center concentration of 50 ppm the yield stress of $KBr_{0.67}Cl_{0.33}$ increased from its unirradiated value of $21 MN/m^2$ to $30 MN/m^2$. Corresponding values for polycrystalline KCl are $26 MN/m^2$ and $37 MN/m^2$.

DD FORM 1473

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Alkali Halides						
Pure and doped KCl						
KCl: KBr mixed crystals						
Flow Stress						
Crystal Growth						
Crystal Characterization						
Irradiated KCl						
Irradiated Polycrystalline KCl						

TABLE OF CONTENTS

I. INTRODUCTION

This project was initiated to study the effects of impurity doping and electron irradiation on the mechanical and optical properties of alkali halides. Our group has concentrated its efforts on KCl, which has been shown to be the most promising material for use in CO_2 laser windows. A significant part of the Oklahoma State University project involves crystal growth. This area may be separated into two broad aims: comparison of mechanical and optical properties of single crystals grown from identical starting material by both the Bridgman and pulling techniques; and comparison of these properties for crystals grown in a particular apparatus using various types of starting material.

A second major area of the project consists of determining changes in mechanical and optical properties of KCl doped with selected impurities, irradiated with 1.5 MeV electrons or treated in one of several other ways. Mechanical properties monitored include the flow stress and the Vickers micro-hardness. The principal optical property investigated is the absorption coefficient at 10.6μm. The latter measurements are carried out in cooperation with AFCRL and other laboratories.

II. CRYSTAL GROWTH

A. Objectives

The crystal-growth phase of this project has two main objectives: 1) to provide single crystals for mechanical and optical measurements of pure, doped, and irradiated KCl. 2) To provide crystals grown by both the Bridgman and pulling techniques from different starting materials in order to determine the effects of these factors. 3) To provide crystals to other laboratories.

B. Crystal Growth Equipment and Procedures

Two crystal pulling systems have been used in this project, and have been previously described in detail.(1) Both are sealed to allow crystal growth in an inert atmosphere which is free from contamination by impurities in the laboratory. Model I utilizes a stainless steel growth chamber, an internal graphite heater, and a ceramic crucible. Model II, with an external furnace, a silica growth chamber, and a pyrolytic graphite crucible should reduce the possibilities of crystal contamination. Currently, the Model I system is being used exclusively for growth of Sr-doped KCl, while Model II is used solely for growth of undoped KCl.

Initially, both the undoped KCl and Sr doped KCl crystals were grown from melts of untreated "Baker Analyzed Reagent" KCl.[†] These crystals had OH^- concentrations of about 0.5μg OH^-/g KCl and absorption coefficients at 10.6μm of about 4×10^{-3} cm^{-1} (2,3) While these crytals were sufficiently "pure" to study mechanical properties and radiation damage, their high absorption at 10.6μm ruled them out for CO_2 laser applications. Hence, to obtain more acceptable materials, a CCl_4 treatment system was installed to process reagent grade KCl. In addition, KCl ingots purified by HCl and Cl_2

[†] J. T. Baker Chemical Company, Phillipsburg, N.J.

treatments were obtained from the University of Utah to use as starting material.

C. Reactive-Atmosphere Processing

1. Equipment and Procedures

Recent work has shown that crystals grown from a KCl melt which was in contact with a halogen-bearing inert gas typically have lower 10.6μm optical absorption coefficients.(4,5) Pastor and Braunstein (6) have developed a technique in which CCl_4 vapor in an Ar carrier gas passes past the melt in a Bridgman crystal-growth system. This method, called Reactive-Atmosphere Processing (RAP) yields crystals having 10.6μm absorption coefficients in the low 10^{-4} cm^{-1} range.(6,7) Their method also has the advantage of simplicity over the more complex HCl/Cl_2 treatment methods reviewed in detail by Rosenberger.(8) Because crystal pullers generally are incompatible with the reactive atmosphere, a modification for pretreatment of reagent grade material has been introduced. Carbon tetrachloride vapor is bubbled through a charge of molten KCl in a separate silica system. Since the bubbling thoroughly mixes the CCl_4 vapor and the molten KCl, the scrubbing reactions should be more complete. When the treatment is completed, the solidified KCl ingot is transferred to the crystal growth system.

This modified RAP treatment is carried out in the system shown in Figure 1. First, a fused silica crucible containing the untreated reagent grade KCl is placed inside a silica chamber. The furnace surrounds the silica chamber so that the KCl is exposed only to silica and CCl_4 vapors in a helium carrier. Dry helium gas passes through the system at about 15 cm^3/min as the KCl is heated and cooled. The furnace temperature is increased 300 C^o/h until the KCl melts and is then held steady at 850 ± 25°C during the RAP run. When the KCl has melted, the silica transfer tube carrying the helium gas is lowered into the melt. Simultaneously, the helium gas is diverted to

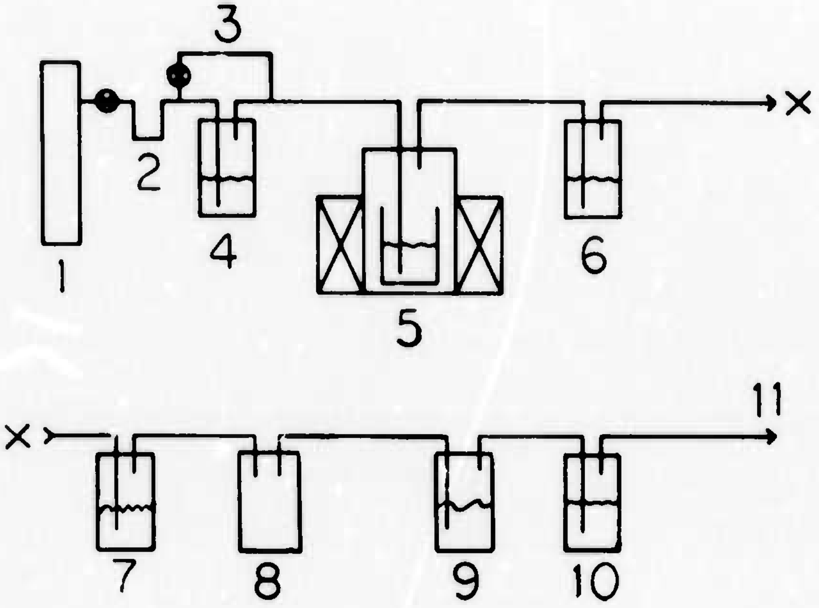

Figure 1. Block Diagram of RAP Apparatus

1. Helium
2. Drying tube
3. Carbon tetrachloride by-pass
4. Carbon tetrachloride
5. Furnace and reaction chamber
6. Empty container
7. Potassium hydroxide (1N)
8. Empty container
9. Ethyl alcohol
10. Water
11. Exhaust

bubble through liquid CCl^4. Hence, CCl_4 vapors come into direct contact with the molten KCl, and the bubbling action of the carrier gas insures good mixing. After the RAP treatment, the tube is pulled from the melt, and helium gas without CCl_4 vapor is allowed to flow through the system until the KCl has cooled to room temperature. The KCl is held in the liquid state for about 15 minutes following the RAP treatment to cause some of the residual reaction products to be carried off by the flowing helium. After the processed KCl has cooled to room temperature, the crucible and KCl are removed, and the solidified boule of KCl, which slips freely from the crucible, is sealed in plastic for later use. The KCl boule often has a small, slightly yellow core which is probably trapped Cl_2 gas.

2. Results and Discussion

KCl crystals have been pulled from melts both of RAP-treated and untreated reagent grade starting material, and of HCl/Cl_2 treated material purchased from the University of Utah. The hydroxyl content of a KCl crystal is easily determined optically and was chosen as the means by which the removal of oxide impurities from the starting material could be monitored. The hydroxyl content, C_{OH}, in μg, OH^- per g KCl, was found from the 204 nm optical absorption band using the relation (9) where A is the optical density at the

$$C_{OH} = 1.31\ A/t \qquad (1)$$

band peak, and t is the sample thickness in cm. The concentration in molar ppm can be found by changing the numerical constant to 5.75. This characterization has a sensitivity of 0.01 to 0.02 μg OH^-/g KCl in a 5 cm long crystal. The absorption coefficients at 10.6μm have been calorimetrically measured for our crystals at other laboratories. For these measurements, the boule ends were water polished flat, and rinsed with isopropyl alcohol. The entire boule was then soaked in concentrated HCl and rinsed in acetone. Table 1 gives the OH^- concentrations, the absorption coefficient at 10.6μm and the treatment process for typical undoped KCl crystals grown here. Also included for comparison are results for high-purity KCl crystals 020565 grown at Oak Ridge National Laboratory.

TABLE I. CRYSTAL CHARACTERISTICS

Boule No.	C_{OH}(μg/g)	$\alpha_{10.6}$(cm^{-1})	(ref)	Starting Material
022873	0.5	0.0042	(3)	untreated
111373	0.03	0.0028	(10)	RAP (45 min)†
022374	not detected	0.0016	(10)	RAP (3 hr)†
112073	0.02	0.001	(10)	UTAH
020565	0.02	0.0008	(10)	grown at ORNL

†Elapsed time for the RAP treatment process.

The data show that RAP treatment of starting material markedly lowers the hydroxyl content of the resulting crystal. In fact, the hydroxyl concentration is invariably lowered by over an order of magnitude, to the detectability limit, in about 1 hour of RAP. These results are consistent with those found earlier by others for HCl/Cl_2 treatment of KCl melts.(4,5) Figure 2 shows the 10.6μm absorption coefficient versus RAP treatment time. The table and figure indicate that RAP pretreatment removes OH^- at a much faster rate than it lowers the 10.6μm absorption. Thus, little, if any, of the absorption at 10.6μm is caused directly by hydroxyl as might be expected. Figure 2 indicates, though, that at least part of this absorption must be caused by one or more impurities which are removed by the RAP treatment. Ion microprobe data presented by Deutsch (11) strongly indicate that an oxygen-containing impurity is involved. The RAP process removes O_2^- and $CO_3^=$ almost as

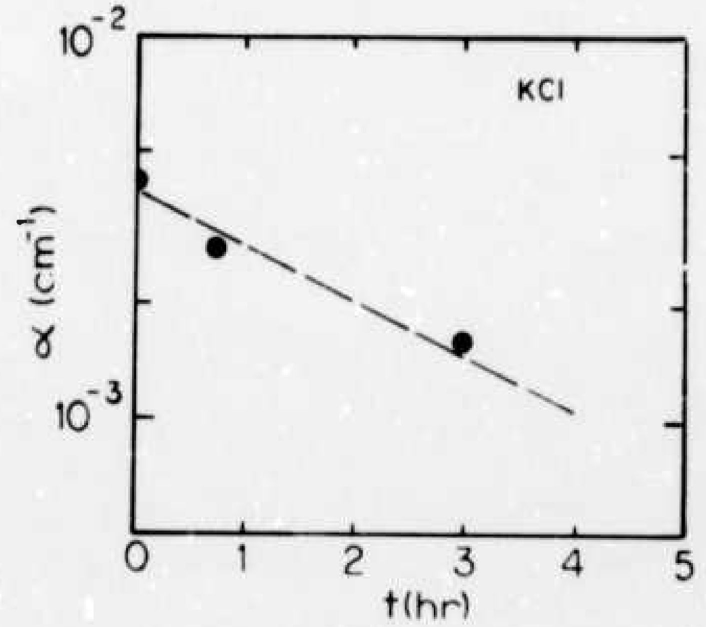

Figure 2. The absorption coefficient, α, at 10.6 μm is shown as a function of the CCl_4 treatment time of the KCl starting material.

effectively as it does OH^-, but some less common oxygen-containing molecular species in the low ppm range could give rise to the observed absorption at 10.6μm. Duthler (12) suggests that the most likely candidates, from the standpoint of their fundamental infrared absorptions, are NO_2^-, HCO_3^-, $SO_4^=$, and $CrO_4^=$. Lipson, Larkin, and Bendow (13) have suggested that either HCO_3^- or ClO_3^- could be the principal absorbing agents, while Deutsch (11) suggests that the Cl-O bond in ClO_4^- is responsible.

A Bridgman system is now being installed in which the RAP treatment will be carried out continuously during the week-long crystal-growth run. Experience of others (13,14) using similar systems indicates that the 10.6μm absorption should be very nearly that expected for the pure bulk lattice.(14)

The authors would like to thank James Harrington for the 10.6μm absorption measurements.

III. MECHANICAL PROPERTIES

A. Overview

Because of its low optical absorption in the infrared, KCl is a prime candidate for CO_2 laser windows. However, window applications require material with greater mechanical strength than that possessed by monocrystalline KCl; hence, it is desirable to develop techniques which increase the yield strength of monocrystalline KCl ($\tau_e \approx 2MN/m^2$) while maintaining a low infrared absorption. Promising hardening mechanisms include: monovalent solid-solution hardening, $\tau_{e\ max} \sim 20MN/m^2$ (15); fine grain boundary hardening, $\tau_{e\ max} \sim 30MN/m^2$ (16,17); and tetragonal defect hardening, $\tau_{e\ max} \sim 10MN/m^2$ (18).

During the past year, hardening brought about by the tetragonal defects introduced by radiation was investigated as a supplement to other hardening mechanisms. Radiation damage appears to increase the yield strength most effectively for the monovalent solid solution and press forged materials. Yield stresses of monovalent, solid solution KCl alloys and press-forged, polycrystalline KCl typically increase from their unirradiated values of $20MN/m^2$ and $26MN/m^2$, respectively, to $28MN/m^2$ and $40MN/m^2$ with defect concentrations of 50 molar ppm. Radiation damage is less effective in strengthening divalently doped KCl. The additional vacancies apparently trap some of the Cl^o ions which ordinarily would have been interstitials. The yield stress of a KCl crystal containing about 100 ppm Sr increases from its unirradiated value of $4.5MN/m^2$ to $9.8MN/m^2$ with a defect concentration of 50 molar ppm. This section describes radiation hardening of a series of KBr_xCl_{1-x} single crystals and forged polycrystalline KCl.

B. Radiation Hardening of KBr_xCl_{1-x}

Tetragonal defects such as divalent impurity ion-vacancy pairs or radiation induced interstitials increase the mechanical flow stress of alkali halide crystals. Fleischer (19) has shown that the interaction between dislocations moving along the slip plane and isolated defects increases the resolved flow stress, τ_r. The increase is given by

$$\Delta\tau_r = \frac{G}{n} C^{\frac{1}{2}} \qquad (2)$$

where G is the shear modulus, C is the mole fraction defect concentration, and n is a number which depicts the hardening effectiveness of the particular type of defect. Fleischer found approximate n values of 10 and 100 for interstitials and divacancies, respectively. Early radiation hardening studies of a number of alkali halides (20,21,22) show a $C^{\frac{1}{2}}$ dependence of the flow stress on F center concentration. However, the F centers alone are not the cause of the change in flow stress (22,23). The strengthening of the irradiated alkali halides is due to the halogen interstitials produced in the radiation damage process.

Recent electron microscope studies of irradiated alkali halide foils by Hobbs, Hughes, and Pooley (24) indicate that interstitials produced during room temperature irradiation either externally with 400 keV electrons or in the 100 keV microscope beam cluster as prismatic dislocation loops. Hence, the hardening is not due to interactions of dislocations and individual interstitials but rather to the interactions of dislocations and interstitial clusters. Their results indicate that the interstitial clusters in KCl are in the form of long needle-like dipole loops which lengthen with increased radiation dosage, the interstitial clusters in KI are rounded and grow radially with increased dosage, and the clusters in KBr are elongated ellipsoids. Hobbs and Howitt (25) have shown theoretically that for the elongated dipole loops in KCl the increase in flow stress is still proportional to $C^{\frac{1}{2}}$:

$$\Delta\tau_r = \frac{Gb}{3k} \frac{2}{(ad)^{\frac{1}{2}}} C^{\frac{1}{2}} \qquad (3)$$

where b, the Burgers vector, equals a/2 <110>, $k \approx 4$ for the dislocation-dipole loop interactions, a is the lattice constant, and d is the dipole width. For KCl they found that the dipole width remained constant for the radiation doses investigated. For systems which form rounded dislocation loops, $\Delta\tau_r$ is expected to be proportional to $C^{\frac{1}{4}}$, and Hobbs and Howitt (25) observed this to be the case in KI. The case of KBr should be somewhat intermediate to KCl and KI.

In this work the flow stress for the KBr-KCl alloy system has been measured as a function of radiation dose. These measurements should provide information on the hardening by interstitial clusters in the transition region between the long, narrow loops in KCl and the elongated, but wider, loops in KBr.

2. Experimental Procedure

The KBr_xCl_{1-x} and KCl samples were cleaved from Czochralski grown boules. The KBr samples were cleaved from material purchased from Harshaw. Since "as grown" mixed KBr-Cl crystals are very brittle, the alloyed boules were annealed for 24 hours at 650°C and cooled to room temperature at a rate of 35 C°/h before testing. Six sets of samples were cleaved from each boule to prepare for irradiation. Each set consisted of one plate (6 mm x 6 mm x 2 mm) which was used for the optical absorption measurements, and six <100> parallelopipeds (1.5 mm x 1.5 mm x 8 mm) which were used for the flow stress measurements. In order to eliminate any possible bleaching effects each set was wrapped in a single layer of aluminum foil, and then was irradiated on both side for various lengths of time in the Oklahoma State University Van De Graaff facility with 1.5 MeV electrons. A beam current density of approximately 1.5×10^{13} electron/s·cm^2 was used.

The flow stress of each of the six bars from each set was measured under compression on an Instron testing machine. The samples were compressed along the <100> direction at a crosshead speed of 0.05 cm/min. This corresponds to a strain rate of about 10^{-3}/s. Some tests were made on unirradiated samples at a crosshead speed of 0.005 cm/min; this slower speed gave the same flow stress result. The engineering flow stress, τ_e, was taken to be the stress value at the intersection of the tangents to the elastic and first plastic flow portions of the curve. The individual flow stresses were averaged to obtain the value reported for each set. In order to compare the results with theory, the resolved flow stress, τ_r, the component of the flow stress parallel to the primary slip direction, is needed. For the alkali halides $\tau_r = \frac{1}{2}\tau_e$.

The radiation dose for each set was determined by measuring the F center concentration, found from the F band optical absorption of the plate sample, with a Cary 14 spectrophotometer. The change in wavelength of the F bank absorption peak with changing composition ($0 \leq x \leq 1$) was in good agreement with the data reported by Smakula, Maynard, and Repucci (26). In agreement with Still and Pooley (27), the coloration rate of the mixed crystals was found to be considerably less than that for either KCl or KBr.

3. Results and Discussion

The resolved flow stress, τ_r, versus the square root of the molar F center concentration, C, for the KBr_xCl_{1-x} system is shown in Figure 3. The resolved flow stress for all compositions is directly proportional to the square root of the F center concentration. However, in some of the materials, a slight softening was observed for low radiation doses. A similar observation was made by Nadeau (22) for a few of the pure alkali halides. The softening occurs during early stage coloration where few stable interstitials are thought to be produced.

Since the flow stress increases as the square root of the F center concentration for all compositions, the interstitial clusters must retain the elongated shape as x varies from 0 to 1 in the KBr_xCl_{1-x} system. The widths of the clusters may be estimated from Equation 3 and the slopes of of the τ_r versus $C^{\frac{1}{2}}$ curves. For the alkali halide's slip system

$$G = [\tfrac{1}{2} C_{44} (C_{11} - C_{22})]^{\frac{1}{2}} \qquad (4)$$

where the C_{aa}'s are the elastic constants. No published elastic constants for the mixed alkali halides are known to exist; therefore, a weighted average of the G's (calculated from tabulated elastic constants) for pure KCl and pure KBr was used. Table II lists the shear moduli and the estimated cluster

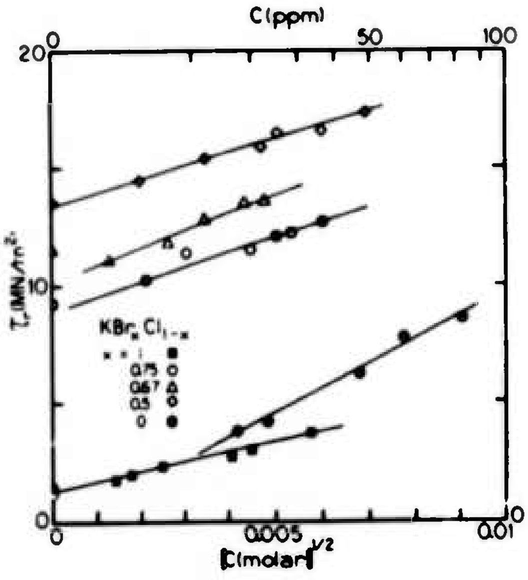

Figure 3. The resolved flow stress, τ_r, is shown as a function of the square root of the molar F center concentration for irradiated KBr$_x$Cl$_{1-x}$ crystals.

widths. The estimated cluster width for KBr is 3 to 4 times that for KCl. This is in reasonable agreement with the electron microscope results (24). Since the mixed crystals are probably somewhat inhomogenous, the d's listed in Table II are not precise; hence, the fact that there is not a smooth transition from KCl to KBr is understandable. However, the general trend of the data is for decreasing cluster widths as x varies from 1 to 0 (KBr to KCl).

4. Summary

The hardening of the mixed crystal system KBr_xCl_{1-x} has been measured as a function of radiation dose. The resolved flow stress increases as the square root of the F center concentration for all samples in this system. This result indicates that the interstitial clusters observed by Hobbs, Hughes, and Pooley (24) retain their elongated character as the alloy system goes from KCl to KBr and, furthermore, that the lengths of the clusters grow with increased radiation dosage.

C. Radiation Hardening of Polycrystalline KCl

1. Introduction

Since crystals deform by the motion of dislocations they may be strengthened by defects which block the motion of dislocations. The flow stress of polycrystalline alkali halides increases as the grain size becomes progressively finer. (16,17) The individual grains of polycrystalline material each have different effective yield strengths and differently oriented slip systems. Because they must remain fitted together during a deformation of the entire sample, the grains must deform nonuniformly. (28) Petch (29) has shown that if dislocation motion is blocked by a grain boundary, the yield strength increase is inversely proportional to the square

TABLE II

Shear Moduli, G, and Cluster Widths, d, for KBr_xCl_{1-x}

x	G(10^3 MN/m^2)	d (Å)
1.0 (KBr)	8.5	18
0.75	8.95	18
0.67	9.13	8
0.5	9.4	11
0.0 (KCl)	10.3	5

root of the average grain size, d; that is,

$$\tau = \tau_0 + kd^{-\frac{1}{2}} \qquad (5)$$

where τ is the yield stress, τ_0 is the yield stress of the single crystal, and k is a property of the material. Equation 5 suggests that if τ_0 were increased, that is, if the original single crystal material were strengthened, then the polycrystalline sample would be strengthened an equivalent amount. Tetragonal defects such as impurity ion-vacancy pairs of radiation induced interstitial clusters have been found to significantly increase the single crystal flow stress of alkali halides. Chin, et al.(30,31) and Sibley et al. (18) have found that KCl crystals doped with Sr^{2+} have a flow stress proportional to the square root of the Sr concentration. This is in agreement with Fleischer's theory (19) for hardening due to tetragonal defects.

Interstitial clusters produced by ionizing radiation also strengthen alkali halide single crystals.(21,22) Sibley and Sonder (21,32) have verified that the radiation damage in alkali halides occurs through an efficient photochemical process. Ionizing radiation removes an electron from a Cl^- which then forms as excited Cl_2^- molecule with a neighbor. This molecule dissociates and initiates a <110> replacement cascade which results in a Cl vacancy with a trapped electron and a Cl^o interstitial some distance away. The vacancy and trapped electron is known as the F center, which has an optical absorption near 560nm in KCl. The F absorption band can be used to determine the F center concentration and, therefore, the interstitial concentration. As mentioned earlier recent electron microscope studies of irradiated alkali halide foils by Hobbs, Hughes, and Pooley (24) indicate that interstitials produced during room temperature irradiation either externally with 400 keV electrons or in the 100 keV microscope beam cluster in the form of prismatic dislocation loops and thus, the hardening is not due to interactions between dislocations and individual interstitials, but rather to the interaction between dislocations and these loops. Hobbs and Howitt (25) have shown theoretically that for the elongated loops in KCl, the increase in flow stress is still proportional to $C^{\frac{1}{2}}$

$$\Delta\tau_r = \frac{Gb}{3k} \frac{2}{(ad)^{\frac{1}{2}}} C^{\frac{1}{2}} \qquad (3)$$

where b, the Burgers vector, equals $\frac{a}{2}$ <110> $k \approx 4$ for the dislocation-dipole loop interactions, and d is the dipole width. For KCl, they found that the width remains constant for the radiation doses investigated. Hopkins <u>et al</u>. (33) have found that Equation 3 holds for radiation hardening of KBr-KCl mixed crystals. For systems which form rounded loops, $\Delta\tau_r$ is expected to be proportional to $C^{\frac{1}{4}}$; Hobbs and Howitt observed this result in KI.

Recently, Becher <u>et al</u>. (34) have found that forged KCl:Sr^{2+} samples show significantly greater yield strengths and that the Petch relation, Equation 5 holds with an increased τ_o. They also found, for some samples, that the slope k, was increased. Because of the possibility of a similar additive hardening due to radiation damage of forged KCl and because of the possibility that the already deformed material may alter the interstitial cluster formation we have investigated the radiation hardening of Polytran polycrystalline KCl from the Harshaw Chemical Company.

2. Experimental Procedure

The polycrystalline KCl used was "Polytran" material supplied by the Harshaw Chemical Company. The average grain size was about 25μm, as determined from photomicrographs of a water-etched surface. Several sets of samples were cut from the original boule using a diamond saw. Each set consisted of 10 parallelopipeds (1.5 x 1.5 x 7.0 mm) which were used for flow stress measurements, and one plate (7 x 5 x 0.3 mm) which was used for optical absorption measurements. The plates were thinned by water polishing after cutting and then polished by immersion in concentrated HCl. Each set was wrapped in a single layer of aluminum foil to eliminate any possible bleaching effects, and irradiated on both sides. The radiation facility used for this experiment was the Oklahoma State University Van De Graaff accelerator. This accelerator supplied electrons of energy 1.5 MeV and a beam current density of 1.5×10^{13} electrons/s·cm^2.

The flow stress of each of the 10 bars from each set was measured under compression on an Instron testing machine. Samples were compressed along the long axis at a crosshead speed of 0.05 cm/min. This corresponds to a strain rate of 10^{-3}/s. The engineering flow stress, τ_e, was taken to be the stress value at the intersection of the tangents to the elastic and first plastic flow portions of the curve. Typical stress versus strain curves for polycrystalline and monocrystalline KCl are shown in Figure 4. Individual flow stresses were averaged to obtain the value reported for each set.

The radiation dose for each set was determined by measuring the F center concentration, found from the F band optical absorption of the plate sample, with a Cary Model 14 spectrophotometer.

3. Results and Discussion

The engineering flow stress, τ_e, versus the square root of the molar F center concentration, C, for irradiated monocrystalline KCl (29) and polycrystalline KCl is shown in Figure 5. These results show that the radiation hardening is independent of the grain boundary hardening, and that the hardening mechanism is not altered by the deformation caused by the forging process. The radiation hardening is additive for the defect concentrations studied. Since the slope of the τ_e versus $C^{\frac{1}{2}}$ curve for polycrystalline KCl is the same as that of the monocrystalline KCl, the widths

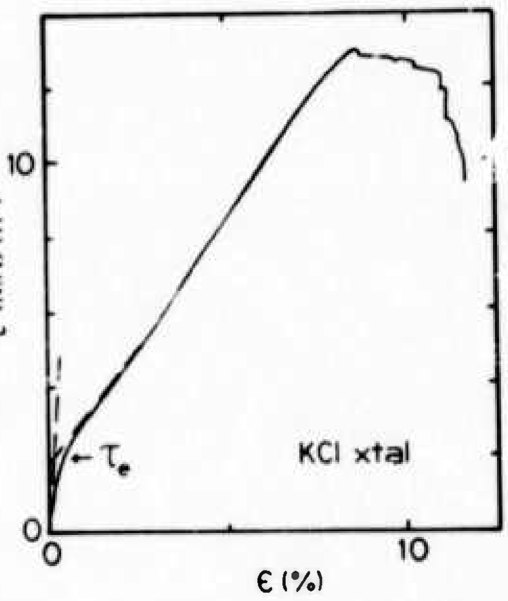

Figure 4a. The stress-strain curve for single crystal KCL is shown.

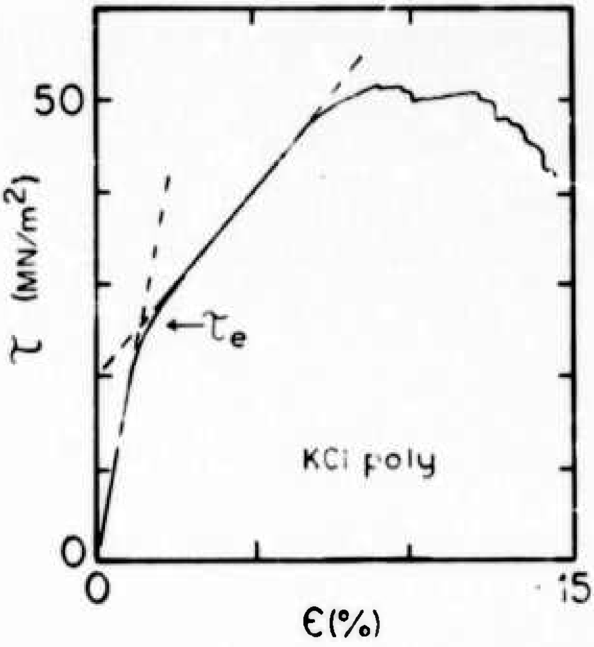

Figure 4b. The stress-strain curve for polycrystalline KCL is shown.

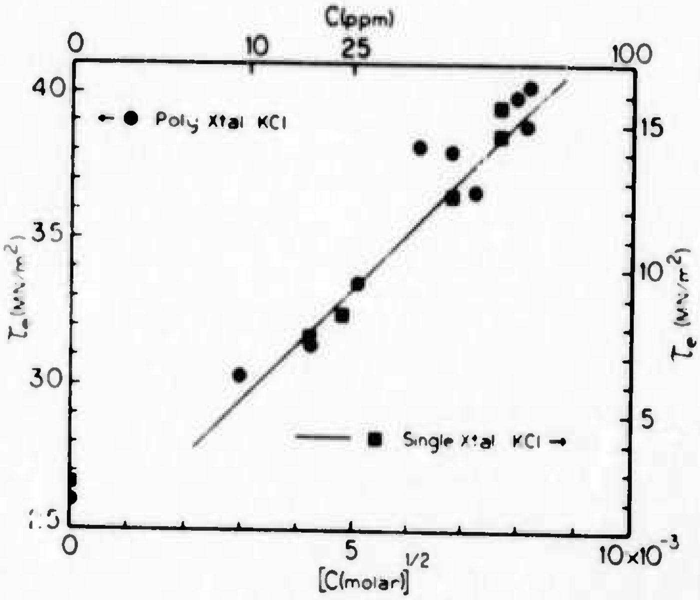

Figure 5. The engineering flow stress for polycrystalline KCl is given on the left hand scale and the engineering flow stress for single crystal KCl is given on the right. Both are shown as a function of the square root of the molar F center concentration.

of the interstitial clusters apparently remain constant and cluster formation is not altered by the polycrystalline nature of the sample. Hobbs, et al.(27) found that the cluster length increased but that the cluster width and density remained constant with increased radiation dose. Their data indicate that the average distance between clusters is ~ 0.1μm and that, for an F center concentration of $5 \times 10^{17}/cm^3$, the cluster lengths are less than 0.1μm. The fact that our studies demonstrated no grain boundary-interstitial cluster interactions, i.e., that the radiation hardening mechanism was unaltered by the polycrystalline nature of the material, is not surprising, since the average grain size for the measured polycrystalline KCl was 25μm. It would be interesting to investigate the effects of ionizing radiation in polycrystalline materials having average grain size ~ 1μm to see if grain boundary-interstitial cluster interactions could be observed.

The authors would like to thank the Harshaw Chemical Company for supplying the Polytran KCl material.

V. SUMMARY

Two crystal pullers of different design are in full operation, and a modified Bridgman apparatus is nearing completion. A Reactive-Atmosphere Processing apparatus suitable for use with crystal pullers has been constructed. Hydroxyl concentrations of crystals grown from material treated by this apparatus are significantly reduced with approximately a one-hour RAP treatment. However, infrared calorimetric measurements indicate that significantly longer RAP times are necessary to remove impurities responsible for the 10.6μm absorption.

Radiation hardening of materials already hardened by other mechanisms has been studied. An interstitial concentration of 50 molar ppm in crystals of the solid solution $KCl_{0.33}Br_{0.67}$ increased the engineering yield stress from an unirradiated value of 20 to 28MN/m^2. The same interstitial concentration in press-forged polycrystalline KCl from a value of 26 to a value of 40MN/m^2. For a crystal containing 200μg Sr^{++} per g KCl, the corresponding values of the engineering yield stress were 4.5 and 9.8MN/m^2 for a 50 molar ppm interstitial concentration.

Publications and Presentations resulting from this work: J. R. Hopkins, "Comparison of Vacancy and Interstitial Hardening in KCl," Phys. Stat. Sol. (a) 18, K15 (1973); J. R. Hopkins, J. A. Miller and J. J. Martin, "Flow Stress, Vickers Hardness, and Wing Size for Pure and Doped KCl and for KCl:KBr Mixed Crystals," Phys. Stat. Sol. (a) 19, 591 (1973); J. R. Hopkins, J. J. Martin, and J. Larkin, "The Effects of Ionizing Radiation on the Hardening of KBr_xCl_{1-x}," J. Appl. Phys. to be published; J. J. Martin, C. T. Butler, J. R. Hopkins, and W. A. Sibley, "Hardening of Alkali Halide Infrared Laser Window Materials," at the 3rd Conference on High Power Infrared Laser Window Materials," Nov. 1973; J. R. Hopkins, J. J. Martin and J. Larkin, "The Effects of Ionizing Radiation on the Hardening of KBr_xCl_{1-x}," at the March Meeting of the American Physical Society.

V. REFERENCES

1. W. A. Sibley, *et al*, Annual Technical Report, AFCRL-TR-73-0342, April 1973.

2. H. Lipson, AFCRL, private communication, 1973.

3. J. A. Harrington and M. Hass, NRL, private communication, 1973.

4. C. T. Butler, *et al*, ORNL Report, ORNL-3906, February 1966.

5. R. Capelletti, V. Fano and M. Scalvine, J. Crystal Growth, **5**, 73 (1969).

6. R. C. Pastor and M. Braunstein, Technical Report, AFWL-TR-72-38, March 1972.

7. P. H. Klein, NRL, Semi-Annual Technical Report, ARPA Order 2031, June 1973.

8. F. Rosenberger, "Purification of Alkali Halides" in *Ultrapurity*, M. Zief and R. Speights, eds., Marcel Dekker, Inc. N.Y. 1972.

9. B. Fritz, F. Lüty and J. Anger, Z. Phys. **174**, 240 (1963).

10. J. A. Harrington, University of Alabama-Huntsville, private communication, 1974.

11. T. F. Deutsch, Third Conference on High Power Infrared Laser Window Materials, C. A. Pitha, A. Armington and H. Posen, eds., November 12-14, 1973, p. 13. AFCRL-TR-74-0085 (I), Special Reports, No. 174, 14 February 1974.

12. C. J. Duthler, J. Appl. Phys., to be published.

13. H. Lipson, J. J. Larkin, and B. Bendow, *loc. cit.* reference 11, Vol. II, p. 237.

14. J. W. Davisson, M. Hass, P. H. Klein and M. Kruhlfeld, *ibid.*, Vol. I, p. 31.

15. Air Force Cambridge Research Laboratory Quarterly Progress Report No. 6, AFCRL-72-0559. Special Reports No. 147, September 1972.

16. R. J. Stokes and C. H. Li in *Materials Science Research*, H. H. Studelmaier and W. W. Austin, ed., (Plenum, N. Y. 1963), Vol. I, pp. 133-157.

17. P. F. Becher and R. W. Rice, J. Appl. Phys. **44**, 2915 (1973).

18. W. A. Sibley *et al.*, Annual Technical Report, AFCRL-TR-73-0342, April 1973.

19. R. L. Fleischer, Acta. Met. 10, 835 (1962).

20. W. A. Sibley and J. R. Russell, J. Appl. Phys. 36, 810 (1965).

21. W. A. Sibley and E. Sonder, J. Appl. Phys. 34, 2366 (1963).

22. J. S. Nadeau, J. Appl. Phys. 34, 2248 (1963).

23. J. R. Hopkins, Phys. Stat. Sol (a) 18, k15 (1973).

24. L. W. Hobbs, A. E. Hughes, and D. Pooley, Proc. R. Soc. Lond. A 332, 167 (1973).

25. L. W. Hobbs and D. G. Howitt, Paper presented at Europhysical Topical Conference on Lattice Defects in Ionic Crystals, Marseille-Luminey, 2-6 July 1973.

26. A. Smakula, N. C. Maynard and A. Repucci, Phys. Rev. 130, 113 (1963).

27. P. P. Still and D. Pooley, Phys. Stat. Sol. 32, k147 (1969).

28. C. S. Barrett, Structure of Metals, McGraw-Hill, N. Y., 1943.

29. N. J. Petch, J. Iron and Steel Inst. (Lond.) 173, 25 (1953).

30. G. Y. Chin and W. L. Mammel, Met. Trans. 4, 335 (1973).

31. G. Y. Chin et al., J. Amer. Ceram. Soc. 56, 369 (1973).

32. W. A. Sibley and E. Sonder, Point Defects in Solids, J. H. Crawford and L. Slifkin, eds. Plenum Press, 1972.

33. J. R. Hopkins, J. J. Martin, and J. Larkin, J. Appl. Phys., to be published, (1974).

34. P. F. Becher, et al., loc. cit. reference 11, Vol. II p. 579.

VI. APPENDIX

KCl Crystals Grown During this Period

Boule No.	Dopant	Starting Material	Use
051673	Sr	Reagent	stock
053073	''	''	thermal conductivity
061373	--	''	''
062073	--	''	AFCRL (absorption test)
062573	--	''	mechanical test
062773	--	''	mechanical test
062973	--	''	stock
070673	--	''	seeds
071373	Sr	''	stock
071773	''	''	''
072873	''	''	''
082473	''	''	''
090473	''	''	''
090673	''	''	''
091373	''	''	Honeywell Corp. Res. Center
093073	--	RAP	stock
100273	--	''	Honeywell Corp. Res. Center
100973	--	''	AFCRL (absorption test)
101673	--	''	stock
102273	--	''	''
102473	--	''	mechanical tests
111373	--	''	U. of Alabama-Huntsville (absorption test)
111573	--	Rosenberger	stock

112073	--	Rosenberger	U. of Alabama-Huntsville (absorption test)
112673	Sr	RAP	stock
112973	''	''	''
120673	--	Reagent	stock
121073		RAP	AFCRL (absorption test)
121273	Sr	RAP	U. of Alabama-Huntsville (absorption test)
121473	''	''	stock
011974	''	''	''
013074	''	''	''
020474	''	''	thermal conductivity
020874	--	Rosenberger	stock
021874	--	''	stock
022274	Sr	RAP	''
022374	--	''	U. of Alabama-Huntsville (absorption test)
031474	Sr	''	stock
031874	--	''	''
041874	--	''	U. of Alabama-Huntsville (absorption test)
042074	--		''