2
To be published in: Proc. 3rd Europhysics
Topical Conference "Lattice Defects in
Ionic Crystals" (J. de Physique, supplement)
Canterbury, England, September 17-20, 1979.

BNL-27014

CONF-7909101--3

RADIATION INDUCED COLOR CENTER AND COLLOID
FORMATION IN SYNTHETIC NaCl AND NATURAL ROCK SALT*

P. W. Levy, K. J. Swyler and R. W. Klaffky[†]

Brookhaven National Laboratory

Upton, New York 11973, U.S.A.

MASTER

*Supported by the U.S. Department of Energy Office of Nuclear Waste
Isolation and the Division of Basic Energy Sciences under contract
EY-76-C-02-0016.

[†]Now at the Los Alamos Scientific Laboratory.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *fy*

Abstract

F-center and colloid particle formation has been studied in synthetic NaCl and natural rock salt crystals with apparatus for making optical absorption measurements during irradiation. F-center and colloid formation are functions of temperature, dose, dose rate, strain applied prior to irradiation and numerous other factors. Many of the observed properties are in accord with the Jain-Lidiard theory for radiation induced F-center and colloid growth above room temperature.

Resumé

On étudie la formation de centres F et de particules colloïdales dans des cristaux naturels et synthétiques de NaCl avec un appareil permettant la mesure de l'absorption optique pendant irradiation. La formation des centres F et des particules colloïdales dépend, entre autres, de la température, du taux d'irradiation et de la dose totale, ainsi que des contraintes appliquées avant irradiation. Beaucoup de propriétés observées répondent à la théorie de Jain-Lidiard pour la croissance des centres F et de particules colloïdale induits par irradiation au dessus la température ordinaire.

I. INTRODUCTION

Radiation induced color center formation in the alkali halides has been studied extensively at or below room temperature but not, in comparative detail, above room temperature. Coloring studies on natural and synthetic rock salt (NaCl) at elevated temperatures are of interest for purely basic reasons and for practical radioactive waste disposal considerations. However, basic radiation effect aspects will be emphasized in this paper.

For three decades or more references to colloid formation have been scattered throughout the color center literature. Space is not available to describe them here. Most of the recent work on radiation effects in natural and synthetic rock salt was undertaken by groups at Oak Ridge National Laboratory and Harwell. Much of the Oak Ridge work, particularly that on stored energy, is described in a widely distributed report (1). Chemical properties of irradiated NaCl have also been investigated (2). The Harwell efforts, which included numerous electron microscope studies, are described in numerous reports and papers (3-6). These studies established many of the general features of radiation induced color center and colloid formation in synthetic NaCl above room temperature. They will be described below, but in the context of the measurements to be described in this paper. The experimental studies, particularly those at Harwell, are the basis of a general theory of color center and colloid particle formation in sodium chloride above room temperature formulated by U. Jain and A.B. Lidiard (7).

II. EXPERIMENTAL TECHNIQUES

All of the measurements outlined below were made with equipment at Brookhaven National Laboratory for making optical measurements on samples during irradiation with 0.5 - 3.0 MeV electrons (Fig. 1), at dose rates in the 10^4 - 10^9 rad per hour range. The optical absorption of the sample, and any radio-luminescence, can be recorded as often as every 40 seconds in the 200-400 or

400-800 nm range. γ absorption measurements in the 400-800 nm region are described here. Luminescence has been observed during irradiation from both natural and synthetic salt samples but has not been studied in detail. The samples are located in a temperature controlled chamber containing inert gas. Even at the highest dose rates, the sample temperature is never more than a few degrees above the chamber temperature. Numerous measurements have been made on both synthetic NaCl crystals and on natural rock salt samples from a variety of geological locations.

III. MEASUREMENTS

The measurements described here were chosen to emphasize the most general features of radiation induced defects formation in NaCl which can be compared to the Jain-Lidiard Theory. Additional details are contained in published or soon to be published papers (8,9).

Measurements made on synthetic NaCl at room temperature are in accord with the results reported in the literature. F-center concentration vs. dose curves, i.e. the growth curves, increase monotonically and appear to be approaching a plateau or a nearly linear curve with pronounced slope. At room temperature, F-center growth in natural rock salt crystals is similar to that observed in synthetic crystals. However, in natural salt F-center growth is accurately described by a (irradiation time)^{1/2} dependency not observed in synthetic crystals.

F-Center and Colloid Formation in the 100-300 C Temperature Range

Radiation induced F-center and colloid growth, in the temperature range where colloid growth is observed, is illustrated by Fig. 2. This figure shows absorption spectra obtained with synthetic NaCl crystals irradiated with electrons at approximately 1.2×10^8 rad per hour and at 150 C. Successive recorded spectra are identified by scan numbers. Qualitative features illustrated by Fig. 2 apply to both synthetic and natural samples throughout the temperature range where colloid growth is observed. A typical F-center growth curve is obtained at low doses. At the dose corresponding approximately to F-center

"saturation" the colloid formation rate increases from a low or negligible value to a rapidly increasing one. Thus colloid concentration vs. dose curves closely resemble classical "nucleation-and-growth" curves which can be specified by an arbitrarily defined induction period and a rapidly increasing segment well approximated by a power law.

The measured absorption in synthetic NaCl near the peak of the F-band, illustrated in Fig. 3, shows three important features. First, as the irradiation temperature increases the "saturation" level decreases. Second, in natural rock salt and above 200 C in synthetic NaCl, the rate at which the F-centers reach saturation increases as the temperature increases. Third, the activation energy for vacancy migration contributing to colloid particle growth, calculated from the measured saturation levels using the Jain-Lidiard theory, is 0.2 eV below 250 C and 0.9 eV at higher temperatures. Comparisons between the data and the Jain-Lidiard theory are summarized in Table 1.

A number of curves showing optical absorption vs. irradiation time, near the peak of the colloid band are shown in Fig. 4. Irrespective of the choice of nucleation and growth parameters, it is found that colloid growth is low at 100 C, increases to a maximum in the 150-175 C range and decreases to a negligible value at approximately 250 C. In synthetic NaCl the rapidly increasing portions of the colloid growth curves are well approximated by a power law of the form t^4 to t^5 , where t is irradiation time. In contrast, in natural rock salt colloid growth curves are well approximated by $t^{2.1}$ to $t^{2.3}$ dependencies. This is one of several results illustrating differences between natural and synthetic rock salt.

Strain or Plastic Deformation Effects

Only results obtained with synthetic crystals irradiated at a fixed temperature and dose rate will be described. Samples were slowly compressed to different strains ranging from zero to approximately 10 percent, prior to irradiation.

This increases the initial F-center coloring rate and decreases the colloid growth curve induction period dramatically, as shown in Fig. 5. This observation strongly suggests, but does not prove, that the nuclei for colloid formation are dislocation related. Natural samples, not strained prior to irradiation, exhibit shortened induction periods that can be explained by assuming the samples were strained by geological forces.

IV. COMPARISON WITH JAIN-LIDIARD THEORY

The results outlined above are compared with selected elements of the Jain-Lidiard theory (7) in Table I. It is apparent that many aspects of the theory are in accord with the observations. Also, there are points of disagreement. Some may be experimental artifacts and others may be removed by slightly modifying the theory.

V. ACKNOWLEDGEMENTS

Extensive discussions with Dr. A.B. Lidiard and Dr. R.E. Bartram are sincerely appreciated.

REFERENCES

1. JENKS, G.H. and BOPP, C.D., Oak Ridge National Laboratory Report 5058 (1977).
2. JENKS, G.H., SONDER, E., BOPP, C.D., WALTON, J.R. and LINDENBAUM, S.,
J. Phys. Chem. 79 (1975) 871.
3. HOBBS, L.W. and HUGHES, A.E., AERE-Harwell Report R8092 (1975).
4. HOBBS, L.W., Surface and Defect Properties of Solids 4 (Chem. Soc.
Specialist Period. Reports, London) (1975) 152.
5. HOBBS, L.W., SAIDOH, M. and ORERA, V.M., Int. Conf. on Defects in Insulating
Crystals Gatlinburg, TN, USA, Oct. 1977 (Oak Ridge National Laboratory,
Oak Ridge) 172.
6. HOBBS, L.W., J. de Physique, Supp. C-9 (1973) 227.
7. JAIN, U. and LIDIARD, A.B., Phil. Mag. 35 (1977) 245.
8. SWYLER, K.J., KLAFFKY, R.W. and LEVY, P.W., Sci. Basis of Nuc. Waste
Management 1 (Plenum, New York) (1979) 349.
9. KLAFFKY, R.W., SWYLER, K.J. and LEVY, P.W., Proc. Int. Symp. on
Ceramics in Nucl. Waste Management: Amer. Ceramic Soc., Cincinnati, OH
(1979), In press.

TABLE 1
SELECTED COMPARISONS WITH JAIN-LIDIARD THEORY

Theory	Synthetic NaCl	Natural Rock Salt
F-centers increase monotonically to a "saturation" level	observed	observed
F-saturation level independent of crystal source and strain	observed	observed
F-saturation level varies as (dose rate) ²	observed	observed
Activation energy obtained from F-center saturation single valued and ~0.4 eV	0.2 eV observed below ~250 C and 0.9 eV above ~250 C	under study
Colloid formation in a restricted temp. range	observed	observed
Colloid formation not observed at low dose rate	not studied	not studied
Colloid induction period dependent on dislocation density	observed: induction period reduced by prior strain	observed: induction period reduced by prior strain
Colloid formation rate in the t^2 to $t^{3/2}$ range	t^4 to t^5 observed in unstrained crystals, $t^{2.1}$ to $t^{2.3}$ observed in highly strained crystals	$t^{2.1}$ to $t^{2.3}$ observed in crystals not additionally strained

FIGURE CAPTIONS

1. Experimental equipment used to study radiation damage in synthetic and natural rock salt samples.
2. Radiation induced absorption spectra in NaCl recorded at four minute intervals during irradiation with 1.5 MeV electrons. The F-center growth is observed immediately after irradiation commences, but rapid colloid growth is preceded by a pronounced induction period.
3. Growth of optical absorption, near the F-center peak, recorded during irradiation of synthetic NaCl. This data has not been corrected for the contribution from the overlapping colloid band.
4. Growth of optical absorption, near the colloid band peak, recorded during irradiation of synthetic NaCl. This data has not been corrected for the contribution from the overlapping F-center band.
5. Colloid band growth curves for synthetic NaCl crystals both unstrained and strained the indicated amounts prior to irradiation.

FIGURE 1

SYNTHETIC NaCl
 1.2×10^8 rad/h
IRRADIATION TEMPERATURE 171 C

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5