Effect of Fractional X-Irradiation of NaCl Crystals on *F*-Center Density

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An attempt is made to verify an effect reported by Lin whereby the *F*-center density in an alkali halide crystal irradiated over only part of its cross section is proportional to the fraction of the crystal exposed to the x-ray beam. These experiments fail to verify Lin's result, and in fact show that, within experimental error, the *F*-center density produced in a crystal exposed to a given intensity of x-rays for a given time is independent of the fraction of the crystal irradiated.

THE linear expansion of NaCl and KCl crystals resulting from x-ray irradiation has recently been investigated by Lin.[1] The results obtained indicate that the fractional change in length, $\Delta l/l_0$, of a crystal irradiated only over part of its cross section is a function of the x-ray dose, but, for a given intensity and irradiation time, is independent of the fraction of the crystal exposed, at least in the range of *F*-center densities below $10^{17}/cm^3$. To account for this result, it was proposed that vacancies are generated by the irradiation uniformly over the entire crystal, including the unirradiated portion.

In view of this proposal, it might be expected that, for equal x-ray exposures, the *F*-center concentration in the irradiated part of the crystal varies in proportion to the fraction of the crystal irradiated. In a group of experiments on KCl crystals, Lin shows data which indicate that the *F*-center concentration is indeed almost proportional to the fraction of the cross-sectional area of the crystal irradiated when this fraction varies from 0.3 to 0.7.

This surprising effect has already led to a proposed modification of the existing theories of vacancy formation during x-ray irradiation.[2] Because of the importance of Lin's results to the theory of color center formation, the authors attempted to repeat the experiment on the effect of fractional irradiation on color center density.

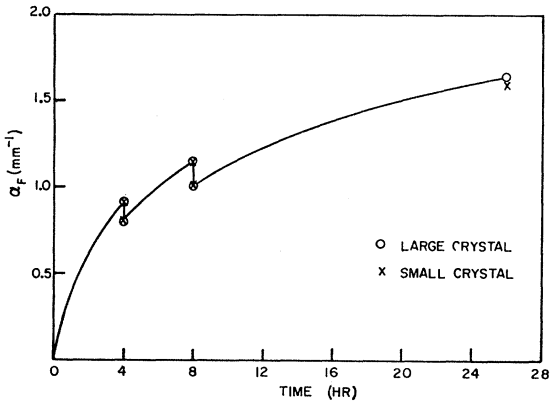

FIG. 1. Variation of absorption coefficient, α_F, with total irradiation time for the large and small crystals. The vertical portions of the curve represent the decrease in α_F when the crystals were maintained in the dark at room temperature for 48 hours between each irradiation.

Two specimens with dimension 8.21×8.35×0.39 mm and 14.62×14.41×0.40 mm were cleaved from a crystal of NaCl supplied by Dr. K. Korth of Kiel, Germany.[3] The x-ray beam used for irradiation was brought through the central hole ($\frac{5}{16}$ in. diameter) of a 2.5-inch long lead cylinder. The specimens were mounted at the end of this cylinder with their large faces perpendicular to the cylinder axis. In this way all but 0.494 cm^2 of the cross-sectional area of the specimen was shielded from irradiation. X-rays from a Cu target, operated at 40 kv and 20 ma, which were filtered through a 1.72-mm thick crystal of NaCl, were used unless otherwise stated. The purpose of the filter was to remove soft radiation which is absorbed very heavily near the surface of incidence of the x-rays, and in this way to produce a nearly uniform coloration of the irradiated crystal. With the above arrangement, the portions of the area irradiated for the large and small specimens were 23.4% and 72%, respectively. These values are comparable to the range investigated by Lin.

Each specimen was given consecutive x-ray exposures of 4, 4, and 8 hours duration. Between each irradiation it was maintained in the dark at room temperature for a period of 48 hours. The optical density at the maximum of the *F* band was measured, in each case, by means of a Beckman model DU spectrophotometer.

The absorption coefficient, α_F, at the maximum of the *F* band, following these various irradiations are given in Fig. 1. It was found, as shown in Fig. 1, that over a range of α_F values up to 16 cm^{-1} (corresponding to an *F*-center concentration up to $10^{17}/cm^3$), both crystals showed, to within experimental error, essentially identical coloration for the same x-ray exposure.

It appeared possible that the disagreement between this result and that reported by Lin might be due to the fact that Lin used unfiltered radiation, which would have produced more intense coloration near the surface of incidence. Since the intense coloration near the surface is believed to represent the second-stage of "slow-type" coloration, which involves a different

[1] Y. Y. Lin, Phys. Rev. **102**, 968 (1956).
[2] J. J. Markham (private communication).
[3] This crystal showed an *F*-band growth curve comparable to that of Harshaw crystals, which were the crystals used by Lin.

mechanism than the first-stage coloration,[4] it was thought necessary to make a comparison of the two crystals when irradiated without a filter. Accordingly, the two specimens used in this investigation were given a further irradiation without a filter for a period of 3 hours. At the end of this irradiation the large and small crystals showed nonuniform coloration and optical densities, $\log_{10}(I_0/I)$, of 0.650 and 0.653, respectively. These values are again in agreement to within the experimental error.

In summary, the present investigation has been unable to verify the result reported by Lin that the F-center concentration in the alkali halides varies directly with the percentage of cross-sectional area of the crystal irradiated. On the contrary, it is shown that the F-center concentration is independent of the fraction of the crystal irradiated.

[4] R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956); A. S. Nowick, Phys. Rev. **111**, 16 (1958), preceding paper.

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Electroluminescence from the Surface Layer of $BaTiO_3$, $SrTiO_3$, and Associated Materials

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Electroluminescence resulting from high-frequency excitation ($\gtrsim$500 kc/sec), has been observed in $BaTiO_3$, $SrTiO_3$, and associated materials. It is shown that the light emission is the result of a high rf field across a thin surface barrier. The efficiency of this emission is very low, and a tentative value of $10^{-6}\%$ was obtained. A model involving field emission from the metal electrode into the crystal surface layer is proposed to explain the observed phenomena. The characteristics of this surface layer are relatively insensitive to temperature, from at least -40°C to 300°C. The ratio of permittivity to thickness, ϵ/L, was found to have a value of $\leq 1.4\times10^5$ cm^{-1} for the $BaTiO_3$ surface layer.

INTRODUCTION

THERE have been many studies of electroluminescence (EL) reported in the literature.[1] The majority of these have been concerned with ZnS or materials considered to have similar excitation and emission mechanisms. However, "recombination" radiation has been observed when semiconductors are biased in the forward direction.[2,3] More recently Newman[4] reported visible light emitted from a reverse-biased silicon p-n junction and proposed that it might result from avalanche breakdown. This was confirmed and extended by Chynoweth and McKay[5] who later found a somewhat different effect which resulted from high-field emission in silicon p-n junctions.[6] Recently the author reported electroluminescence in $BaTiO_3$.[7]

The surface layer on $BaTiO_3$ has been studied by a number of investigators.[8–12] Reported values of the thickness and dielectric constant of the surface layer have varied widely depending on the method of measurement.

It is the purpose of this paper (1) to present experimental data on electroluminescence from $BaTiO_3$ and $SrTiO_3$, (2) to establish the most probable mechanism of this light emission, and (3) to use these data to determine the ratio of the permittivity to thickness of the surface layer. The experimental apparatus has been described elsewhere.[13] Therefore, only recent modifications will be included in this paper.

EXPERIMENTAL RESULTS

(a) General Observations

EL has been observed from barium titanate, strontium titanate, and associated materials, when they were excited with rf voltages. The optimum output was achieved when the electrodes were applied in a concentric configuration as previously described.[13] This arrangement produced a high field around the small center electrode. All of the light was observed to originate from this region, apparently coming from the electrode-crystal interface. Most of the light was emitted with uniform intensity around the perimeter, or at times over the entire area of the small electrode. However, there were generally a few tiny spots that were more intense than the surrounding emission.

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