PHOTODISSOCIATION OF OH^- IONS IN RbCl CRYSTALS

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Experiments utilizing optical absorption techniques in the visible and ultraviolet spectral regions have been performed to study the primary and secondary defects from the photodissociation of the OH^- in RbCl crystals in the presence of CN^- over the 77–300 K temperature range. Due to the presence of the CN^- molecular impurity it was observed that these ions interact with the OH^- impurities changing the photodissociation process. Experimental results allowed us to propose new aggregate defects. These defects are complex centers in the form of $[OH^- \cdot CN^-]$ characterized by an electronic absorption at 1940 Å and a vibrational-rotational absorption at 2165 cm^{-1}, and in the form of $[O^- \cdot CN^-]$ with a characteristic electronic absorption at 2040 Å. One property of the complex center $[OH^- \cdot CN^-]$ observed is that it allows photodissociation of the OH^- impurity, by X and UV irradiation, at room temperature producing U and $[O^- \cdot CN^-]$ centers. The additive coloration of the RbCl:OH^- + CN^- also showed that it's possible to obtain U centers directly from the dissociation of the complex $[OH^- \cdot CN^-]$.

INTRODUCTION

Substitutional OH^- impurities in alkali halides are photodissociated under UV irradiation below 100 K. In general, the following reaction is observed:

$$\boxed{OH^-} + h\nu \rightarrow H_i^0 + \boxed{O^-}$$

The efficiency of this process is in general constant in the range from 6 to 300 K. The different photochemical processes observed at different temperatures within this range are due to different thermal stabilities of the photoproducts and their aggregates that are involved in this process.[1] This process however can be altered if CN^- ions are present in the sample. Very little is known about the interaction of OH^- and CN^- impurities in codoped samples in spite of the fact that individually speaking these impurities and their properties were extensively studied in alkali halides. The objective of this work was to verify phenomenologically the basic OH^- photodissociation mechanisms that take place when CN^- impurities are also present in the crystal.

EXPERIMENTAL

Low temperatures at the samples were obtained with a 8 DT Janis Optical Cryostat. This cryostat was provided with a heat exchange chamber as a thermal switch for the continuous production of temperatures between 70 and 300 K and for the application of pulsed annealings. Optical absorption data were obtained with a Cary 17 D spectrophotometer. Monochromatic UV light irradiation was made with a 1000 watts Hanovia Xenon lamp heat filtered and dispersed by

Cryst. Lattice Defects and Amorphous Mater., 1987, Vol. 17

interference filters. Additive and radiative colorations were performed with usual laboratory techniques.

OH^- Photodissociation in RbCl : OH^-

The OH^- UV absorption in RbCl is a structureless band that peaks at 2137 Å with a FWHM of 0.60 eV, that is slightly reduced at low T. Under UV resonant irradiation at 77 K one observes its intensity reduction followed by the appearance, in a one to one ratio, of two other bands centered at 2450 Å and at 1930 Å which are assigned to H_i^0 (U_2 centers) and O^- substitutional centers, respectively (Figure 1). Following this photodissociation, the application of heat pulses generated a sequence of secondary products[2,3] like H_2O^- (stepwise at 105 and 130 K), and others (U and F center) originated by the thermal dissociation of the H_2O^- itself again in a stepwise behaviour that produced U centers at 180 K and F centers at 240 K. This type of behaviour was previously seen in KCl : OH^- and other alkali halides and extensively studied in its intrinsic and extrinsic

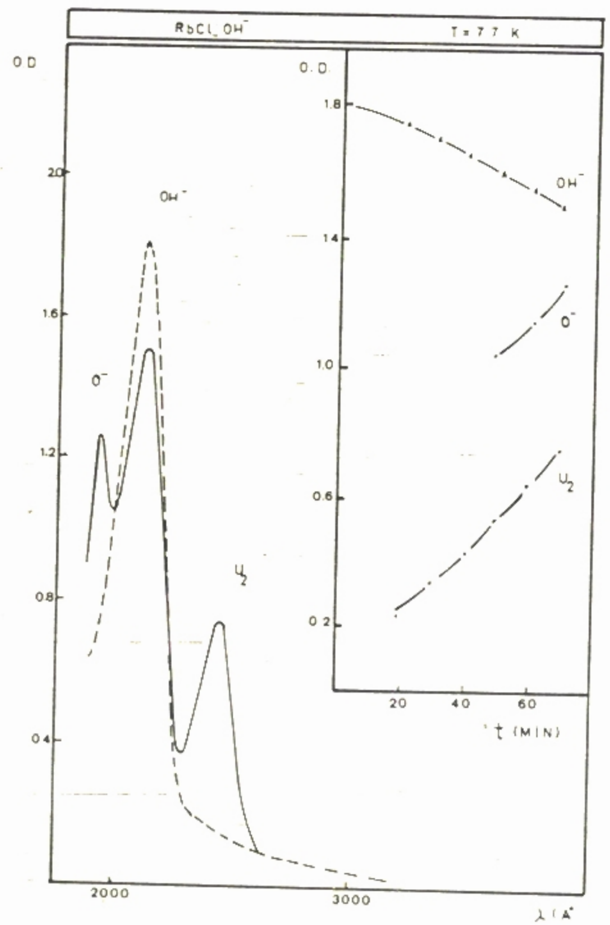

FIGURE 1 UV absorption spectra of RbCl : OH^- before and after UV irradiation. Increase and decay of OH^-, U_2 and O^- absorption bands as a function of UV irradiation time.

thermal generation of secondary products that followed the OH^- photodissociation. Some of the main processes can be summarized by the following equations:[4]

$$2H_i^0 + \boxed{O^-} + KT \rightarrow \boxed{H_2O^-}$$

$$H_i^0 + \boxed{OH^-} + KT \rightarrow \boxed{H^-} + OH_i^0$$

$$\boxed{e^-} + (H_i^0)^* + OH_i^0$$

$$(H_i^0)^* + \boxed{OH^-}$$

$$\boxed{O^-} + (H_i^0)^* \rightarrow \boxed{OH^-}$$

where $(H_i^0)^*$ stands for thermally unstable U_2 center and OH_i^0 stands for a neutral OH interstitial, the box □ indicating substitutional defects.

OH^- Photodissociation in RbCl : OH^- + CN^-

Samples of OH^- and CN^- in codoped RbCl crystals showed, besides the OH^- UV absorption band, another UV absorption at 1960 A at RT (1940 A at LNT) tentatively attributed to a CN^- perturbed OH^- absorption or $[OH^- \cdot CN^-]$. This band was associated with another absorption at 2165 cm^{-1} (~4, 6 μ) in a region where IR bands due to CN^- occur.

Under the same UV irradiation conditions that were applied to RbCl : OH^- samples, the RbCl : $OH^- + CN^-$ exhibited a totally different behaviour. The OH^- and the 1940 Å absorptions were reduced and two other bands appeared; one due to H_i^0 centers, peaking at 2450 Å and another at 2040 Å not due to O^- absorption that is centered at 1930 Å in RbCl (Figure 2). This process might be represented by the following reactions:

$$\boxed{OH^-} + [OH^- \cdot CN^-] + h\nu \rightarrow H_i^0 + 2040\text{ Å band}$$

A similar process of OH^- photodissociation with H_i^0 center formation accompanies the overall process as shown in the insert of Figure 2. However the normal O^- absorption that has an oscillator strength big enough to overcome the absorption coincidence with the $[OH^- \cdot CN^-]$ band (O^- at 1930 Å and $[OH^- \cdot CN^-]$ at 1940 Å) does not show up. This fact by itself, although analysed only under a phenomenological point of view, leads to a similar hypothesis of a CN^- perturbed O^- center, or $[O^- \cdot CN^-]$ like it was established for the $[OH^- \cdot CH^-]$ center.

The H_i^0 bands resulting from both processes – from OH^- and $[OH^- \cdot CN^-]$ photodissociation – apparently do not show a perturbed behaviour. However the final concentration of H_i^0 derived from $[OH^- \cdot CN^-]$ centers is higher than in the first case. This leads us to propose two independent processes described by:

$$\boxed{OH^-} + h\nu \rightarrow H_i^0 + \boxed{O^-}$$

$$[OH^- \cdot CN^-] + h\nu \rightarrow H_i^0 + [O^- \cdot CN^-]$$

Thermodynamical Follow-up of $[OH^- \cdot CN^-]$ Photoproducts

As the morphology of the $[OH^- \cdot CN^-]$ and $[O^- \cdot CN^-]$ centers and their dissociation/association dynamics are not known, we derived a sequence of

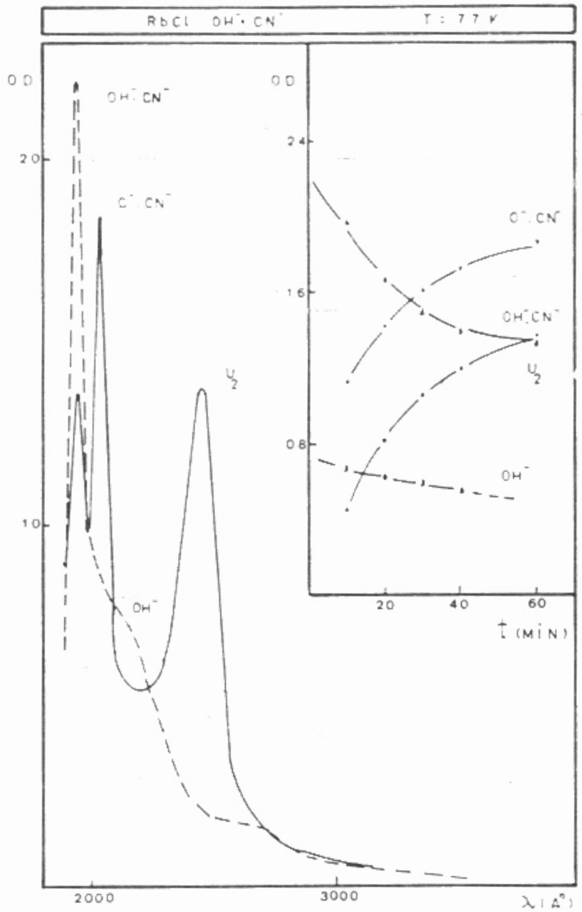

FIGURE 2 UV absorption spectra of $RbCl:OH^- + CN^-$ before and after UV irradiation (2137 Å). Increase and decay of $[OH^- \cdot CN^-]$, OH^-, $[O^- \cdot CN^-]$ and U_2 absorption bands as a function of UV irradiation time.

experiments that would allow to shed more light on the influence of the CN^- ion in the OH^- photodissociation process. Pulsed thermal treatments to produce an evolutive cycle of OH^- products were performed and it was observed that similarly to $KCl:OH^-$ and to $RbCl:OH^-$, H_i^0 are thermally destroyed as expected. Simultaneously one observes the decay of the $[O^- \cdot CN^-]$ and the increase of the relative absorption of other aggregates like the H_2O^- center.[2,4]

According to what was observed and based on previously established models for $KCl:OH^-$, in the range of 80 to 120 K the following reaction could be established:

$$[O^- \cdot CN^-] + H_i^0 + KT \rightarrow [OH^- \cdot CN^-]$$

At higher temperature ranges several effects occur simultaneously and as an attempt to probe the several species that are present, the introduction of F centers is highly desired. It is well known that in the presence of F centers OH^- photodissociation products that are thermally unstable have a higher possibility of becoming trapped and stabilized.[5]

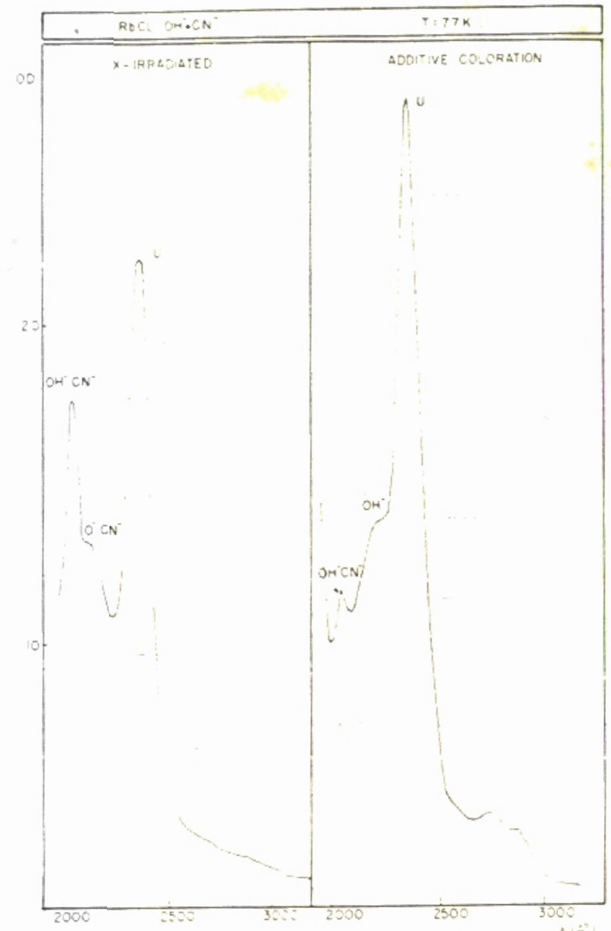

FIGURE 3 UV absorption spectra of additively colored and X irradiated $RbCl:OH^- + CN^-$ crystals.

Probing $RbCl:OH^-$ and $RbCl:OH^- + CN^-$ with F Centers

The introduction of F centers in these samples initially by additive coloration was realized with the intention of trapping the $[O^- \cdot CN^-]$ defect and create a new specimen that could be identified and studied. However it was verified that the additive coloration eliminated the $[OH^- \cdot CN^-]$ band and directly formed U centers. By additive coloration of $RbCl:OH^-$ samples, however, the OH^- band remained unchanged as in $KCl:OH^-$.[5] To eliminate the possibility that the additive coloration process itself was responsible for the destruction of the $[OH^- \cdot CN^-]$ defects through chemical reactions, we produced F centers by X irradiation at room temperature. The same $[OH^- \cdot CN^-]$ destruction and U center generation effects were observed in this case (Figure 3).

All these results were analysed within the framework of normalized concentrations for the several defects involved. Since the proposed model is based on the interactions of the two molecular defects OH^- and CN^-, F centers are in some way responsible for the direct breakdown of the $[OH^- \cdot CN^-]$ complex that leads, in both cases of coloration, the formation of U centers. U centers in these cases are directly formed by the stabilization of H_i^0 centers that are trapped by F centers. The following equation describes this effect:

$$[OH^- \cdot CN^-] + F \text{ centers} \rightarrow U \text{ centers} + [O^- \cdot CN^-]$$
$$T \geqq 300\,K$$

In RbCl:OH^- additive and radiative coloration produces F centers but the OH^- concentration always remains constant. In the radiative coloration case at RT, X rays break up the OH^- molecule but the products are very unstable so one has a reversible reaction that restores the OH^-.

The utilization of F centers confirmed the proposed model of aggregates like $[OH^- \cdot CN^-]$ and $[O^- \cdot CN^-]$. Evidently, other techniques and studies are necessary to check the morphology of these perturbed centers as well to investigate their optical properties, which were beyond the scope of this work. By proposing these defects we tried to demonstrate the enormous possibilities for the genesis of new defects just by departing from codoped crystals with different molecular ions that allow photodissociation and that aggregate and disaggregate by thermal activation.

REFERENCES

1 S. P. Morato and F. Luty, *Phys. Rev. B* **22**, 4980 (1980).
2 L. Gomes and S. P. Morato, *Solid State Commun.* **41**, 653 (1982).
3 S. P. Morato and L. Gomes, *J. Physique* **41**, C6-155 (1980).
4 S. L. Baldochi, Master Thesis University of São Paulo, 1985. Unpublished.
5 S. P. Morato and L. Luty, *J. Phys. Chem. Solids* **41**, 1181 (1980).

Cryst. Latt. Def. and Amorph. Mat., 1987, Vol. 17, pp. 199–204
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OPTICALLY INDUCED REORDERING OF A... CLUSTER DEFECTS IN SEMIINSULATING G...

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The EL2 level in GaAs has been associated with the existence of arsenic rich aggregates. Th... characterized by the existence of a metastable state, which is induced by optical excitatio... temperature ($T < 120$ K). The recovery of the normal state cannot be accomplished b... excitation. However, a recovery of the photoconductivity signal is observed. The analys... phenomenon reveals the existence of more than a metastable state induced by 1–1.25 eV ... These results are discussed on the basis of an optically induced reordering of the arsenic rich a... when the As_{Ga} antisite donors are photoionized. Small differences in the As_{Ga} complexes i... aggregates will produce significative differences in the metastability.

I INTRODUCTION

Seminsulating GaAs is a very important material, which is used as a subs... microelectronics technology. The main midgap level ensuring the compe... of the background shallow acceptors is the so-called EL2 level. In the last... great controversy has been raised about this level. In spite of many invest... devoted to this exciting problem, the confusion about both its physico-c... nature and its properties is great today. Although several years ago... assumed to understand the way this level works,[1] but not its nature, to... discovery of different metastable transfromations of this level has shado... knowledge about it.[2,3,4] EL2 is typically characterized by an optically ... transition into a metastable state, labeled EL2*,[1,5] which changes the pr... of the material as long as it remains in such a state. EL2 is known ... stoichiometric defect associated with the excess of arsenic in the melt,[6] ... not unanimity about its nature, however the hypothesis of a point ... practically ruled out in the actuality,[7] and the possibility it was an amorph... aggregate becomes more reliable.[4]

This paper deals with the photoconductivity properties of the me... configuration of EL2. Different aspects related with the metastability of th... Section III, have to be answered in order to improve the knowledge of ... for the understanding of the EL2 nature. In Section II the experimenta... will be briefly depicted. Section IV deals with the experimental results ... for the photoconductivity of both the normal and the metastable state... Section V is devoted to the discussion of the results.

II EXPERIMENTAL SET-UP

The samples used for the measurements were cut from either Cr-doped h... Bridgman (HB) or undoped LEC (Liquid Encapsulated Czochralski) ing...