PHOTOCHEMISTRY AND REACTIONS OF OH DEFECTS AND

F CENTERS IN ALKALI HALIDES

Spero Penha Morato and Fritz Luty

PHOTOCHEMISTRY AND REACTIONS OF OH⁻ DEFECTS AND

F CENTERS IN ALKALI HALIDES

Spero Penha Morato and Fritz Lüty

CENTRO DE PROTEÇÃO RADIOLÓGICA E DOSIMETRIA
Área de Materiais Dosimétricos

INSTITUTO DE ENERGIA ATÔMICA
SÃO PAULO - BRASIL

INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11.049 (Pinheiros)
Cidade Universitária "Armando de Salles Oliveira"
SÃO PAULO   —   BRASIL

PHOTOCHEMISTRY AND REACTIONS OF OH⁻ DEFECTS AND

F CENTERS IN ALKALI HALIDES[1]

Spero Penha Morato[2] and Fritz Lüty[3]

ABSTRACT

Additively colored KCl:OH⁻ crystals showed under a combined UV and VIS irradiation, a nearly complete and irreversible destruction of all F centers and visible absorption in the crystal. Only upon heating the crystal above 660°C the F center coloration becomes partially restored. The photodissociation of the OH⁻ (under UV light) together with the photoionization of the F center (under VIS light) produces a net effect where all the F centers are converted into U centers. These photoreactions produces high contrast visible images that are completely stable under light at RT. Besides the optical information storage aspect of this effect these photoreactions can also be used for controlled production of U_A centers if the crystal also contains a foreign metallic impurity such a Na⁺ ion.

1 – INTRODUCTION

Substitutional OH⁻ ions in alkali halides under optical excitation of their UV absorption undergo a photodissociation which leads to several primary and secondary photoproducts as already reviewed in our previous works[1,2] (part I and II). Color center and impurities in ions crystals that give rise to photochemical reactions have become recently important possible applications as photochromic media for optical information storage. The photochemical reactions involving OH⁻ and F centers that will be treated in this work make this process very attractive for optical information storage since it allows our (invisible) UV light bleaching process appear as a light contrast bleaching effect in the visible range.

2 – EXPERIMENTAL PROCEDURE

The introduction of F centers into the KCl:OH⁻ crystals was done with the intention to extend this study into the dynamics of the OH⁻ photodissociation products and subproducts. F centers are the simplest defects that can be extrinsically added in large quantities (up to 10^{19} cm⁻³) in alkali halides by a monstoichiometric excess of alkali metals. It is an excellent probe to test the behavior of other centers like H_i^0 through their interactions and recombinations. Our experimetnal procedures therefore consisted, in each temperature range, of a study of the OH⁻ photodissociation in pure KCl:OH⁻ crystals, followed by a subsequent study where we repeated the same procedures with KCl:OH⁻ crystals containing F centers. In this way it was possible to make a direct comparison between the two systems and analyze the role played by the F centers. The same previously experimental techniques[1,2] were used in the present work.

3 – RESULTS AND DISCUSSION

3.1 – Low Temperature Process

In the presence of F centers, the optical photodecomposition of OH⁻ at low temperatures shows basically the following spectral changes: a decrease of the OH⁻ and an increase of the H_i^0 (U_2) band (Figure 1); additionally one observes a decrease of the F band. In Figure 2 we plot these spectral changes versus the irradiation time, and in Figure 3 we compare the OH⁻ decrease with the U_2 band increase, all this for both KCl:OH⁻ and KCl:OH⁻ + F crystals and at 6K and 77K as well. In the KCl:OH⁻ crystal containing F centers, the decay of the OH⁻ band is not affected by the presence of F centers (Figure 2). However, the H_i^0 center growth curve indicates a smaller (also temperature independent) quantum efficiency compared to the "pure" KCl:OH⁻ crystal. In Figure 3, we plotted the OH⁻ band decrease vs. the U_2 band increase and again obtained a straight line with a bigger slope compared to the "pure" KCl:OH⁻ crystal. One may conclude from this fact that the same amount of OH⁻ center destroyed in both systems brings, in the presence of F centers, less H_i^0 centers than it did in the "pure" KCl:OH⁻ crystal. A careful analysis of the number of H_i^0 and F centers involved in this process showed that the amount of F center reduced during the OH⁻ photodissociation process correspond quantitatively to the difference between the H_i^0 centers produced in the two crystals, namely KCl:OH⁻ and KCl:OH⁻ + F. This indicates that in both cases the same OH⁻ → H_i^0 conversion takes place, but that in the presence of F centers part of the created H_i^0 centers react with part of the available F centers.

After the observation of these effects an immediate question arises: What is formed out the H_i^0 and F centers which are consumed in this process? Two evident answers may be anticipated: either the created interstitial hydrogen atom, while moving away from the dissociated OH⁻ state gets captured by a nearby F center, thus creating the H⁻ center (U band); or an F center ionization takes place in the process and the freed electron will meet a stabilized H_i^0 center and from the H_i^- center (U_1 band). The first possibility is clearly excluded, because no trace of the (high oscillator strength) U band is observed in this process. The weak and very broad U_1 band from H_i^- interstitials is much harder to detect. We could however confirm the presence of the second process by illuminating (after the UV photodissociation) with visible light into the F band (see Figure 1). In doing so, we obtained a further concentration reduction for both F and H_i^0 centers (Figure 1). We therefore assume that already, during the UV irradiation, some F centers will be ionized (by irradiation into their conductive states[3] [L bands]) and electrons are transferred to and captured by the H_i^0 center, forming H_i^- centers. The observed photochemical reactions to the KCl:OH⁻ + F system can then be summarized by the following equations:

$$\boxed{\text{OH}^-} + h\nu \rightarrow \boxed{\text{O}^-} + H_i^0 \tag{1}$$

$$\boxed{e^-} + h\nu \rightarrow \boxed{} + e^- \tag{2}$$

$$\boxed{e^-} + H_i^0 \rightarrow H_i^- + \boxed{} \tag{3}$$

3.2 – Thermal Annealing Above 120K

The primary reactions in the presence of F centers described by the above equations, postulate the production of H_i^- centers. As the electronic absorption (U_1 band) of these centers is hard to detect experimentally, we set up an experiment to directly observe the formation of the H_i^- center local mode in this process. The spectral changes in the UV and visible range during the initial OH⁻ photodecomposition are shown in Figure 4. In the insert of Figure 4, we display the rise of the H_i^- center local mode transition. This further confirms the validity of the equations 1, 2 and 3 describing

the primary photoreactions appearing in the same experiment. Adding these equations we obtain for the net reaction:

$$\boxed{OH^-} + \boxed{e^-} + h\nu \rightarrow \boxed{O^-} + \boxed{} + H_i \tag{4}$$
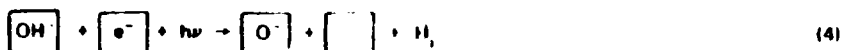
If we pulse anneal this photodecomposed system to 150K (Step 3 in Figure 4) we observe a strong increase of the H_i^- local mode band and a decrease in the F band (besides the thermal destruction of the U_2 band). The thermal annealing process makes the H_i^0 mobile and possibly when it gets conveniently close to the F center, the F center ground state electron will tunnel to the H_i^0 center which is thermally stable. It is interesting to note that in these reactions – and in the ones previously discussed for the KCl:OH$^-$ + F system – interstitial hydrogen atoms never react with F centers to form an H$^-$ defect, a process which would appear to be very natural. Apparently, whenever a mobile H_i^0 defect approaches an F center, a transfer of the F ground state electron to the interstitial hydrogen takes place at a certain distance (possibly by tunneling), forming and stabilizing the H_i^- defect. We never observed the reaction:

$$\boxed{e^-} + H_i^0 \text{ (mobile)} \rightarrow \boxed{H^-} \tag{5}$$

but always instead the electron transfer reaction:

$$\boxed{e^-} + H_i^0 \text{ (mobile)} \rightarrow \boxed{} + H_i^- \tag{6}$$

As a final procedure we pulse annealed our system from 150K to RT (Step 4, Figure 4). Above 200K, H_i^- centers are no longer stable. They will become mobile and eventually be trapped by their anti center – the anion vacancy – and form the H$^-$ center. This process can clearly be observed in Figure 4. We then obtain the reaction:

$$H_i^- + \boxed{} + KT \rightarrow \boxed{H^-} \tag{7}$$
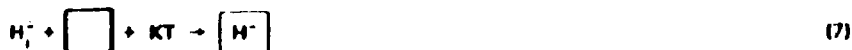
After this last process was completed we observe that the amount of F center reduction corresponds to the amount of U centers created. This fact confirms the above proposed equations to describe our observations. Adding all the equations that recombine the OH$^-$ initial photodecomposition with the final thermal processes up to RT we end up with the net reaction:

$$\boxed{OH^-} + \boxed{e^-} + h\nu + KT \rightarrow \boxed{O^-} + \boxed{H^-} \tag{8}$$

3.3 – Processes at 150K

To study the photodecomposition of OH$^-$ centers at 150K in the presence of F centers we basically repeated with KCl:OH$^-$ + F systems the experiments described in the previous paper[2] Part II. Now, in the presence of F centers the OH$^-$ photodecomposition process produces directly and very efficiently the destruction of F centers (see Figure 5) and the formation of H$^-$ and H_i^- centers. The presence of F light added to the UV irradiation basically does not influence the F decay process as can be seen in the insert of Figure 5. This fact led us to conclude that the tunneling process of the electron to a passing by H_i^0 center is the most predominant process

rather than an F center photoionization process. We should consider here that the formation of the H_2O^- center is taking place simultaneously, but due to the relatively small oscillator strength of the H_2O^- band[4], only very small changes in shape of the F band tails were observed.

3.4 – Room Temperature Processes

At room temperature special care had to be taken to avoid any visible light while irradiating with monochromatic OH^- light since even small exposures to visible light would very efficiently aggregate F centers into F_2, F_3, etc. To achieve this desirable spectral purity of our UV light, we used two monochromators in tandem with a deuterium light source (low intensity visible light output).

The consequent loss in intensity was compensated by a prolonged UV exposure. The results of this experiment are presented in Figure 6B. We see in Steps 1 and 2 that the pure UV exposure is directly responsible for a partial conversion of F into U centers (no F center aggregation was observed at this stage). This is the same net process summarized by Eq. 7. The OH^- photodissociation of the KCl:OH + F system, thermally annealed to RT (e.g., curve 3 in Figure 4) produces a similar net result as direct photodissociation at RT. A subsequent short time F light exposure of the crystal (Step 3 in Figure 6B) produces immediately F center aggregation, a totally independent and well known process that did not bring any change to the UV spectrum. The same original KCl:OH + F crystal, when exposed at RT to the full undispersed irradiation of a Xenon lamp, showed initially that the process described in Eq 8 was indeed taking place. After an appropriate irradiation time ~ 4.5 hours (Step 3 in Figure 7) - one obtains an almost complete destruction of all F centers and visible absorption in the crystal (shown in Step 3, Figure 3?). Now if the undispersed irradiation is extended further for prolonged times, new photochemical processes take place: in the UV range the U-band is bleached and transformed into a new unidentified absorption band in higher energies, while in the visible range, the formation of a colloid band[5] is observed. It was not our intent to study and try to understand these high temperature photoreactions in any detail. They were undertaken after the detailed and quantitative low temperature photochemistry study, to obtain a qualitative survey about the following high temperature photochemistry.

The role of the F centers as extra reaction and trapping sites in the OH^- photochemistry can be summarized as follows: at low temperatures, where basically all primary and secondary reactions products of the OH^- dissociation are thermally stable, the extra F centers have little influence on these reactions. Towards higher temperatures, with increasing instability of the OH^- reaction products, the role of the F center as trapping or reaction sites becomes more and more decisive. At RT, in fact, the OH^- photodecomposition (not present in the pure crystal), becomes possibly only by the presence of F centers. The observation and understanding of the highly efficient F center bleaching effect by UV light in KCl:OH crystals opens another line of possibilities: for potential applications of color centers in optical information storage and to the production of U-aggregate centers. We will now briefly discuss these possibilities.

## 3.5 – Optical Information Storage

Pure additively colored crystals are well known for their stability against a permanent bleaching of their coloration. Under visible light alone, these systems, shows the reversible $F \rightarrow F'$ reaction at low temperatures[6] and the aggregation into complexes F_2, F_3 etc., at high temperatures[7]. When irradiating with visible light into F center systems that also contain OH^- impurities, no new effects are observed. We again obtain the reversible $F \rightarrow F'$ conversion at low temperatures and the F center aggregation at high temperatures. These properties, however, change drastically in KCl:OH crystals if our irradiation contains UV light as we showed in this work. Under OH^- light irradiations, we were able to produce in a very broad temperature range an almost complete and irreversible destruction of F centers and any visible absorption in the crystal under UV light irradiation. This bleaching effect was partially reversible only after heating the samples to 650°C when we observed a return of part of the F centers.

In Figure 8 summarize the decay of the F centers vs. UV irradiation time for several temperatures of study. We see that this process has a small bleaching quantum efficiency at temperatures where H_i^o centers are thermally stable. The maximum bleaching occurred at 150K. At room temperature, although we had an initially high efficiency, the process satured relatively fast. These mixed KCl:OH$^-$ + F crystals therefore allow us to make a UV light irradiation process visible by the bleaching of color (absorption band) in the visible spectral range. It is evident that this ability makes this crystal system interesting as a photochromic material for the storage of optical information. This general field has received in the last decade a lot of attention: three-dimensional "Bragg-angle holograms" have, for instance, been stored in large numbers by optical alignment of F_A centers in KCl:Na$^+$ crystals[8].

To demonstrate qualitatively in the simplest way these photochromic properties of the KCl:OH$^-$ + F material under UV irradiation, we produced some images in these crystals by a simple shadow process. The obtained contrast is remarkably high (60:1) and the images are stable at room temperature and normal light (containing no far components). In Figure 9 we display several different patterns obtained with these crystals under different temperature conditions. The finnest grid structure used a density of 1200 "images" per cm^2. (the resolution of this grainless photochromic material is basically unlimited). However the reversibility of this process is only partial. Under annealing to high temperatures (650°), only part of the original F centers are restored. This does not encourage the use for repeated "write-read-erase..." application as required for computer memory. Nevertheless, this material appears excellent to optically register permanent planar or volumetric information carried by UV irradiation. With the present advent of UV lasers, holographic information storage in these systems may be a definite possibility.

3.6 – Controlled Production of U_A Centers

If our KCl systems contains, besides the OH$^-$ and F centers, metallic impurities such as the Na$^+$, we are able to convert F centers almost entirely into F_A centers, according to the following equation:

$$\boxed{e^-} + \boxed{Na^+} \rightarrow \boxed{e^- \mid Na^+} \qquad (F_A) \qquad (9)$$
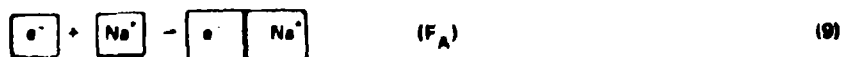
Proceeding with the OH$^-$ photodecomposition at 150K in such a crystal with F_A centers and then annealing to room temperature, we were able to end up with U_A (a substitutional hydrogen ion having a Na$^+$ impurity as one of the nearest neighbors). Their effective net process can be described by the following equation:

$$\boxed{e^-} + \boxed{Na^+} + \boxed{OH^-} + h\nu + KT \rightarrow \boxed{O^-} + \boxed{H^- \mid Na^+} \qquad (10)$$
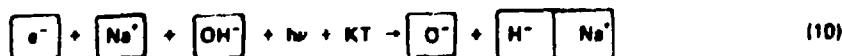
An indication for the presence of this process is displayed in Figure 10. The nearest neighbor metallic impurity reduces the O_h cubic symmetry into C_{4v}, resulting in a splitting of the three-fold degenerate U center local mode transition into a singlet and a doublet[9]. In Figure 10 is displayed the "γ_1 line" attributed to the E_g double degenerate mode. This first rough experiment demonstrates the possibility to create '' centers in a controlled way (so far, U_A centers were observed only statistically in heavily doped crystals with metallic impurities and U centers). This method for creating U centers with locally reduced symmetry (even optically aligned ones!) appears to be very promising for further local mode studies.
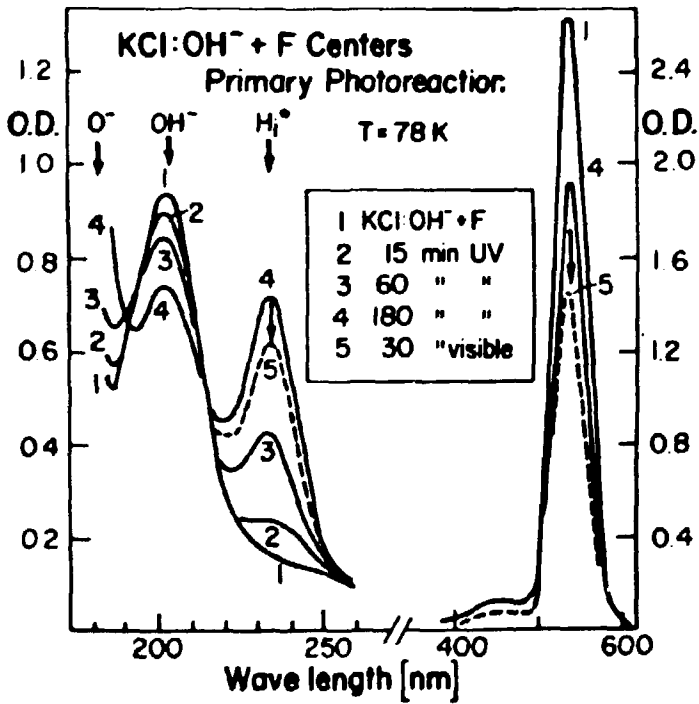
Figure 1 — Optical absorption spectra of a KCl:OH⁻ crystal containing F centers, the primary products of OH⁻ photodecomposition in the presence of F centers and the F center reduction after different UV irradiation times at LNT. The dashed line shows further reduction of F and U₂ bands after subsequent F light illumination.
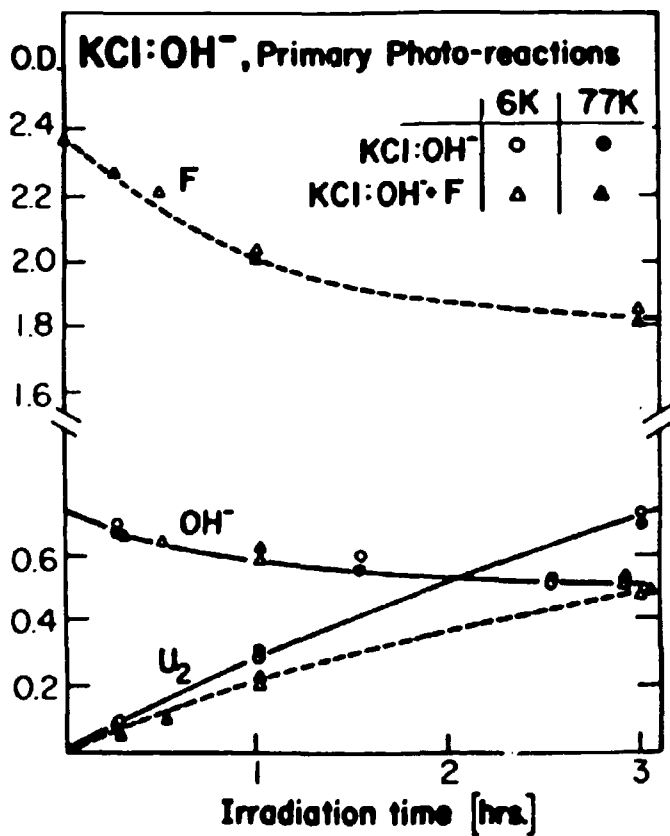
Figure 2 — Build up and decay curves for OH⁻, F and U₂ bands involved in the primary OH⁻ photodecomposition process at 6K and 77K
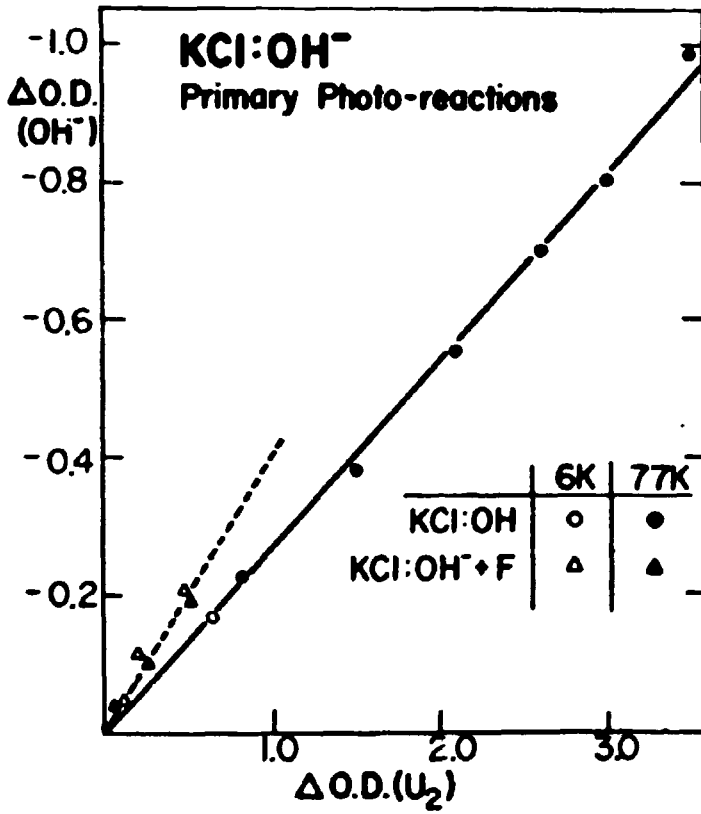
Figure 3 — Plot of the OH⁻ absorption band decrease vs. U_2 band increase at LHe and LN temperatures for both systems KCl:OH⁻ (solid line) and KCl:OH⁻ + F⁻ (dashed line) obtained during the OH⁻ photo dissociation process.
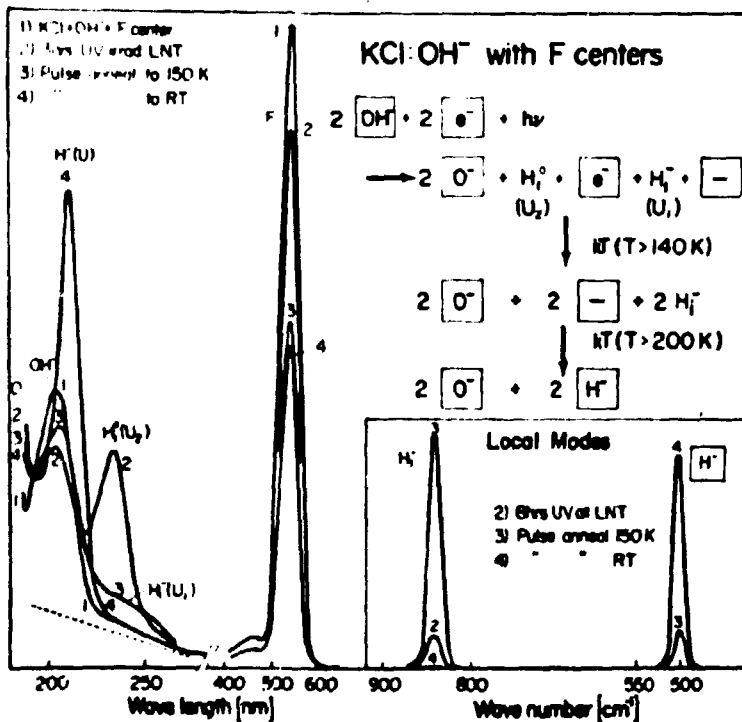
Figure 4 — Thermal annealing processes of a previous OH⁻ photo-dissociated KCl:OH⁻ + F system at 77K. Insert: Hydrogen center (H_i and H) local mode transitions.
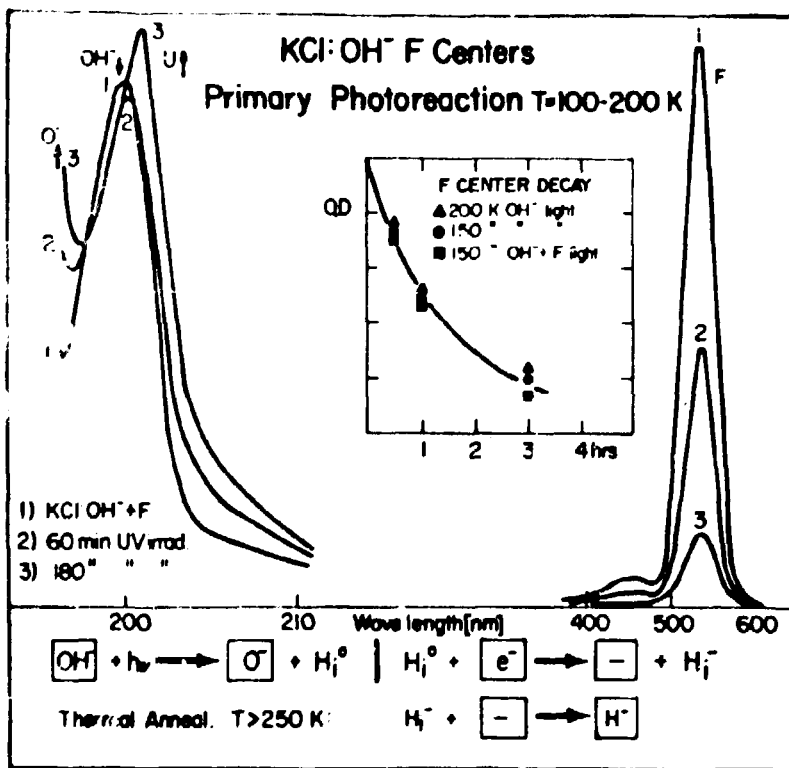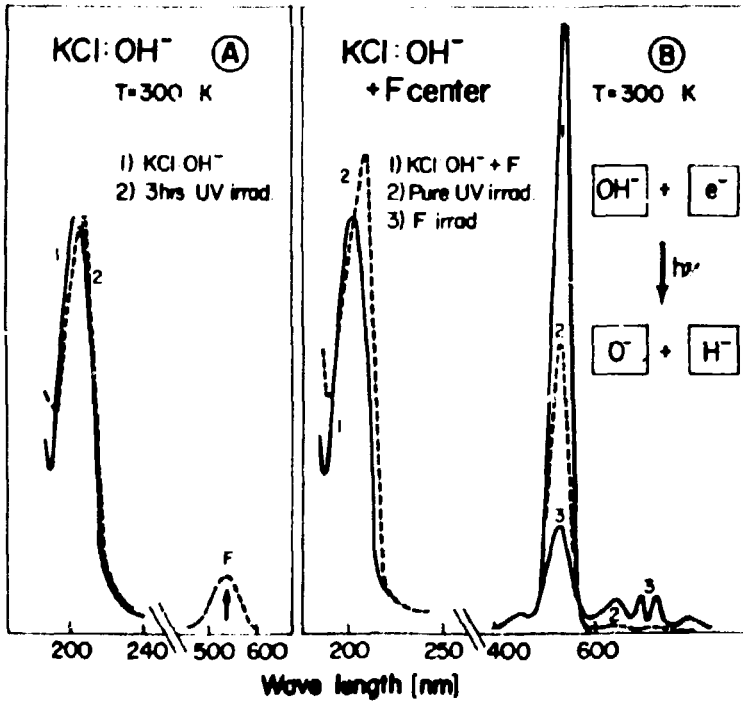
Figure 6 A — UV irradiation of a KCl:OH⁻ system at room temperature.

B — 204 nm (tandem monochromators) UV irradiation of a KCl:OH⁻ + F system at room temperature (measured at 77K)
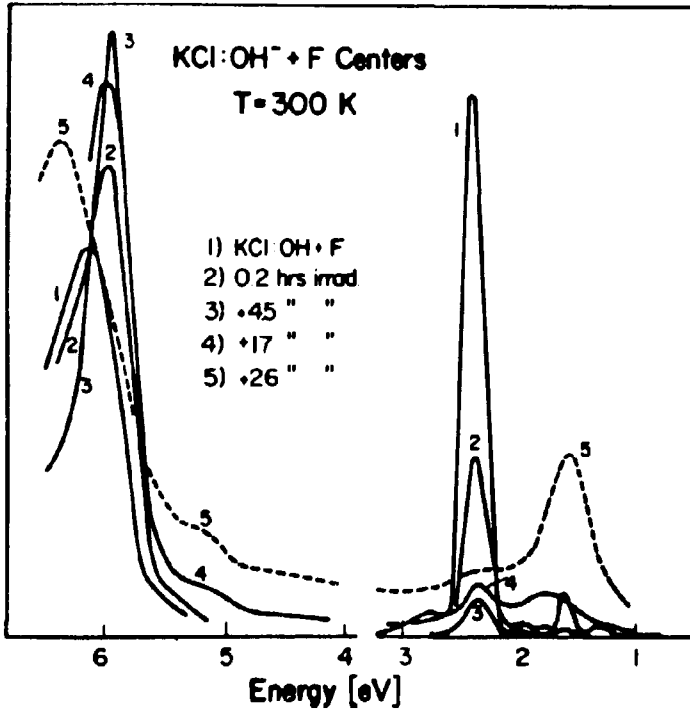
Figure 7 — KCl:OH⁻ + F system under full Xenon lamp irradiation at room temperature (measured at 77K).
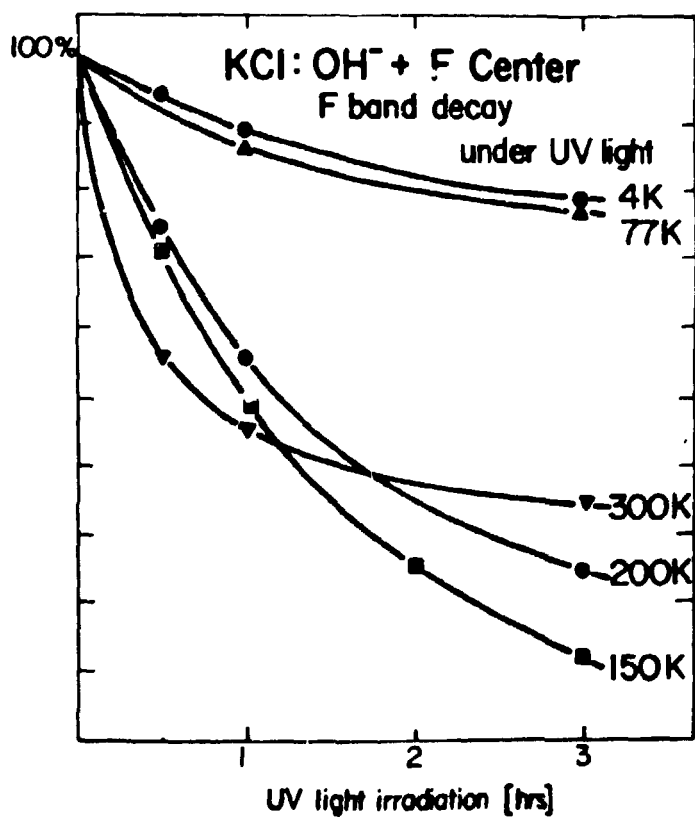
Figure 8 — F center decay curves in a KCl:OH⁻ + F crystal under OH⁻ light irradiation for different temperatures.
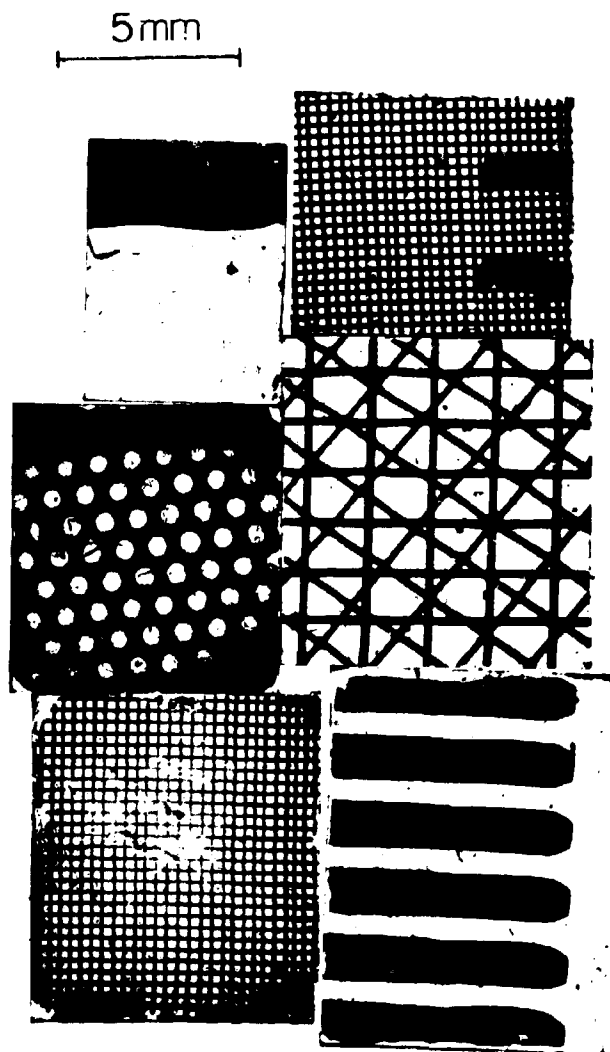
Figure 8 – Photograph of an array of six KCl:OH⁻ + F samples in which we produced different forms of high contrast visible images. Clockwise from the upper left: | 1 | High contrast (60:1) produced by full Xenon lamp irradiation and annealed to RT. | 2 | Same as | 1 |. | 3 |, | 4 |, | 5 |, and | 6 | were produced at RT under full Xenon lamp irradiation.

U_A-Formation in KCl(Na$^+$) from OH$^-$ Photo-dissociation

$$\boxed{e^-} + \boxed{Na^+} \xrightarrow{h\nu} \boxed{e^- \,|\, Na^+} \; (F_A)$$

$$\boxed{e^- \,|\, Na^+} + \boxed{OH^-} \xrightarrow{h\nu} \boxed{O^-} + H_i^- + \boxed{- \,|\, Na^+}$$

$$\downarrow kT$$

$$\boxed{O^-} + \boxed{H^- \,|\, Na^+} \; (U_A)$$

U

3

OH$^-$

2

UV

visible

F_A

2

3

1) KCl·Na·OH$^-$
2) UV irrad 150 K
3) Pulse ann. RT

U_I

2

3

IR

phonon-side-bd.

U_A

U

3

2

200   250   400   600   850   800   550   500

Wave length [nm]   **Wave number [cm^{-1}]**

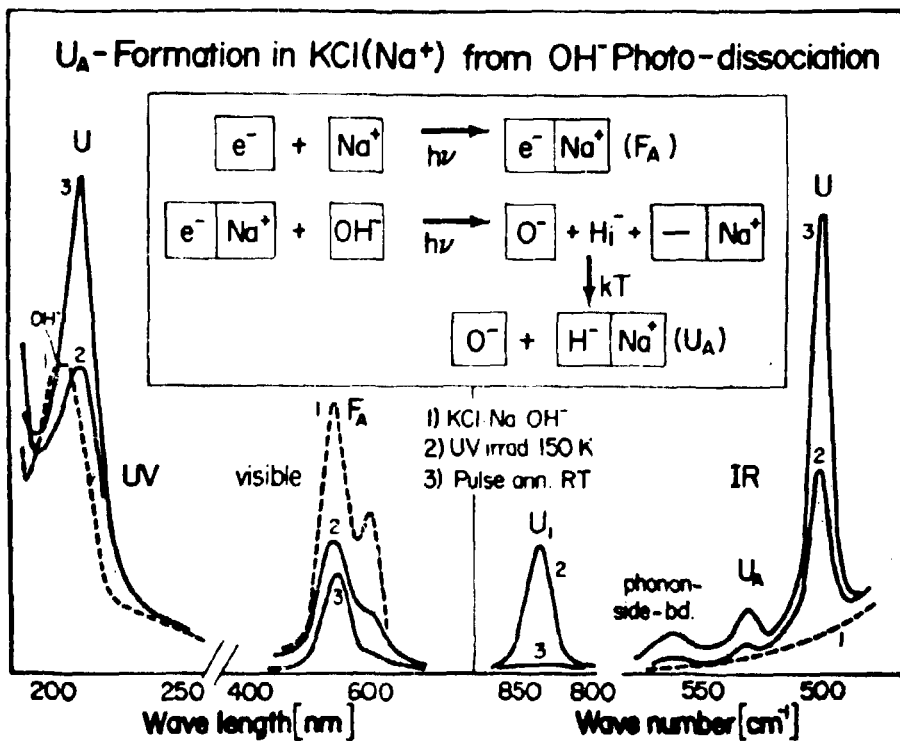**Figure 10** — U_A center formation in a KCl·OH$^-$ + Na$^+$ + F system obtained after the following steps:

a) F → F_A conversion at 15°C.

b) OH$^-$ photodecomposition at 150K.

c) Anneal to room temperature (measurements at 77K).

RESUMO

Cristais de KCl:OH⁻ coloridos aditivamente submetidos a radiação combinada UV o visível mostraram uma destruição quase completa e irreversível de todos os centros F e da absorção visível do cristal. Somente após o aquecimento do cristal acima de 650°C a coloração F foi restaurada parcialmente. A fotodestruição do íon OH⁻ (sob luz UV) juntamente com a fotoionização do centro F (sob luz visível) produz um efeito final onde todos os centros F são convertidos em centros U. Estas reações fotocromicas produzem imagens visíveis de contraste forte que são completamente estáveis sob luz à temperatura ambiente. Além do aspecto de armazenamento óptico de informação estas reações fotocromicas podem também ser utilizadas para a produção controlada de centros U_A caso o cristal contenha impurezas metálicas como Na⁺.

REFERENCES

1. S. P. Morato and F. Lüty. Publicação IEA 506.

2. S. P. Morato and F. Lüty. Publicação IEA 507.

3. F. Lüty, Zeitz f. Physik 160, 1 (1960).

4. L. Gomes and S. P. Morato to be published.

5. A. B. Scott and L. Bupp, Phys. Rev. 79, 341 (1950).

6. H. Fedders, M. Hunger and F. Lüty, J. Phys. Chem. Solids 22, 299 (1961)

7. F. Seitz, Rev. Mod. Phys. 18, 384 (1946).

8. F. Lüty in "Physics of Color Centers" Chapter 3.

9. D. N. Mirlin and I. I. Reshina, Soviet Phys. Sol. State 8, 116 (1966).