Optical effects by high energy electrons in additively colored KCl and KBr crystals

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Radiation effects of high energy electrons on pure and additively colored (AC) KCl and KBr crystals have been studied by optical absorption in the 200-800 nm range at RT. Besides the main F-center related absorption band at 553 nm, the F_2^+ (670 nm) and F_2 (740 nm) bands (R_1 and R_2 centers in old notation) ascribed to F centers aggregates in additively colored KCl are clearly observed. After electron irradiation with energy of 1.0 MeV and doses of 100 kGy or 3.5 MeV and 180 kGy, the F_2^+ and F_2 bands are strongly diminished, the intensity of the F bands is increased and its peak lightly shifted to low energy at 558 nm. In KBr, the related absorption band maximum for the pure and AC samples after irradiation shows the same peak position as the F-center absorption. For AC KBr the intensity of this peak versus accumulative doses shows a maximum around 300 kGy but in pure KBr the peak continuously increases. In contrast, KCl does not show such dependence on accumulative doses. For both samples, the electron irradiation induce at least two bands in the 210-300 nm (UV bands) range that has been related with hole centers (V bands). The results have been analyzed in terms of surface close F centers and alkali and halogen ions desorption processes.

Keywords: Electron irradiation; radiation damage; alkali halides; color centers; F centers.

Efectos por irradiación con electrones de alta energía en cristales puros y coloreados aditivamente (CA) de KCl y KBr se han estudiado a temperatura ambiente por absorción óptica en el rango 200-800 nm. En cristales de KCl aditivamente coloreados, además de la banda de absorción más importante, en 553 nm asignada a centros F, también se observan las bandas F_2^+ (670 nm) y F_2 (740 nm) adscritas a agregados de centros F (centros R_1 y R_2 en la vieja notación). Después de la irradiación con electrones con energía de 1.0 MeV y dosis de 100 kGy ó 3.5 MeV y 180 kGy, la intensidad de las bandas F_2^+ y F_2 disminuye fuertemente y a la vez la intensidad de la banda F incrementa y su posición se desplaza ligeramente en dirección de menor energía, a 558 nm. En KBr, después de la irradiación, el máximo de la bandas de absorción para los cristales puros y CA muestran la misma posición de pico que la banda de absorción relacionada con el centro F. Para cristales de KBr CA la intensidad de este pico versus dosis acumulada, muestra un máximo alrededor de 300 kGy pero en cristales puros de KBr el máximo de la banda continuamente incrementa. En contraste, KCl no muestra tal dependencia sobre la dosis acumulada. Para ambas muestras la irradiación con electrones induce al menos dos bandas en el rango 210-300 nm (UV bands) que han sido relacionadas con centros de hoyo (bandas V). Los resultados se han analizado en términos de centros F cercanos a la superficie y procesos de desorción de iones alcalinos y halógenos.

Descriptores: Irradiación con electrones; daños por radiación; halogenuros alcalinos; centros de color; centros F.

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1. Introduction

Radiation effects in alkali halide (AH) crystals have extensively investigated in the past, mainly in connection with the development of materials for energy production and radioactive waste. During the last decade, the interest in radiation damage in AH have been renewed because this is a method to produce microstructural defects and color centers, which results in materials with novel and unusual properties, particularly in submicrometric and nanoscale dimension[1-3]. It is well known that in electron and photon irradiated AH the principal effects are the creation of several types of defects such as F and H centres, F-centre clusters, etc. Color center clusters and colloids can also be produced by additive coloration or ionizing radiation. When the clusters are formed of several hundreds of F centers, they show a metallic behavior and actually are small alkali inclusion (colloids)[4] which form alkali islands on the surface of the crystal [5,6]. In 1.0 keV electron irradiated KBr and NaCl [7] small islands of rectangular shapes have been reported. The islands develop from small desorption pits, and after high radiation dose the pits became connected and islands are form. The desorption process in alkali halide is explained from the production of mobile F* (excited F center) and H centers which can diffuse independently through the crystal [8]. The finding of Kolodziej *et al.* [7], suggests that desorption pits are formed when the F center concentration in the crystal is high. In that case, small F-center aggregates in the surface can initiate the pits formation.

Because the initial concentration of F centers appears to be important to begin desorption processes as well as pits and colloids formation, in this work we study the optical absorption of additively colored KCl and KBr under high energy electron irradiation. The results confirms that pre-existence of F centers before irradiation affects in both crystals the desorption process and pits formation.

2. Experimental

KCl and KBr crystals were obtain by cutting different size samples from commercially (ESPI) large crystals. Single crystals were not subject to any procedures to obtain clean and well-ordered surfaces and not particular orientation be considered. The additive coloration was achieved by putting large samples of KCl and KBr on a potassium metal atmosphere at 500°C during 24 hrs. After that, the crystals were cleaved in air to get smaller colored samples. Colored additively samples were handling with some exposition to environmental light but shielded for that with a 1.0 mm thick aluminum sheet during irradiation. Electron irradiations were performed with a 1.0 and 3.5 MeV, from a Dynamitron Electron Accelerator. Doses are calculated using radiochromic dye films previously calibrated with a polystyrene calorimeter. Following the irradiations, absorption measurements were carried out with a UV-visible Spectrophotometer Lambda 18 (Perkin-Elmer). Scanning electron microscopy (SEM) images were obtained by electron microscope JEOL 5410 LV.

3. Results

Optical absorption spectra of KCl crystals are shown in Fig. 1. For AC samples, the spectrum shows three well develop absorption bands with maxima at 553, 680 and 740 nm, as they had been previously observed in x-ray irradiated or additively colored samples and then photo stimulated with related F-band light [9]. Actually, these bands are well known and they are ascribed to F (an electron trapped in an halogen vacancy), F_2^+ (an electron trapped in two halogen vacancies) and F_2 (two electrons trapped in two halogen vacancies) centers, respectively [9,10]. Several other very low intensity bands are observable for wavelengths lower than 400 nm, but they are not considered here because the electron irradiation has not appreciable effect on them. Then, after irradiation with electrons of 3.5 MeV to a dose of 180 kGy, the F_2^+ band is bleached and the F_2 band is strongly diminished (broken line, Fig. 1). Simultaneously, the peak of the F-related absorption band is shifted to 558 nm and a new band is induced in the UV region around 215 nm. As in x-irradiated alkali halide crystals, the presence of this band suggests the presence of intrinsic hole defects like V_3 centers (molecular halogen) [11]. In pure KCl the electron irradiation induced very similar absorption bands as in AC irradiated samples but the F_2 band is lightly more intense and the F_2^+ is absent. Optical absorption spectra of pure and AC KBr crystals under electron irradiation of 3.5 MeV to a dose of 180 kGy are shown in Fig. 2. The jagged shape in the main absorption band corresponds to a saturation effect of the spectrophotometer. The solid line just begins to show that effect but still it is possible to observe a maximum around 625 nm, as in the not saturated chain line. This band was report previously as related with F centers in x-ray irradiated and additively colored KBr crystals [10]. The solid line corresponds to a non-irradiated AC crystal and the broken line to the same AC irradiated sample. In both cases, the behavior is very similar and in addition to the saturated main peak, two very low intensity bands are observed in the UV region peaked around 230 and 275 nm. The positions being very close to that reported for U and U_2 centers in KBr crystals at 228 and 272 nm, respectively [12]. In a like manner, electron irradi-

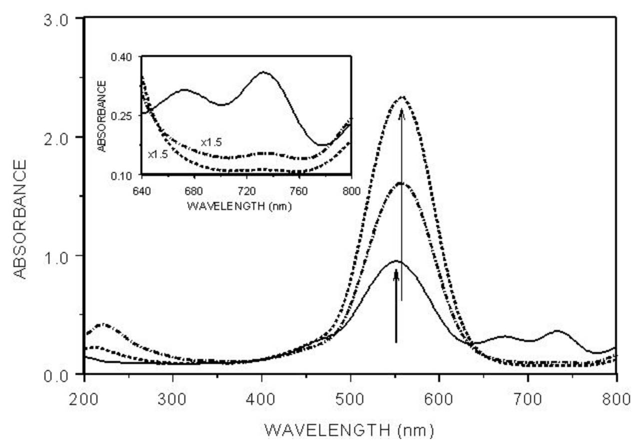

FIGURE 1. Optical absorption spectra of KCl crystals for pure electron irradiated (chain line), AC electron irradiated (broken line) and no-irradiated AC (solid line) samples. Inset shows the expanded F_2^+ and F_2 absorption region.

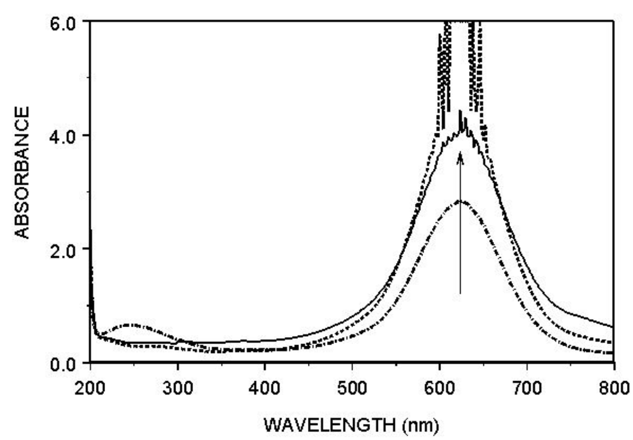

FIGURE 2. Optical absorption spectra of KBr crystals for pure electron irradiated (chain line), AC electron irradiated (broken line) and no-irradiated AC (solid line) samples.

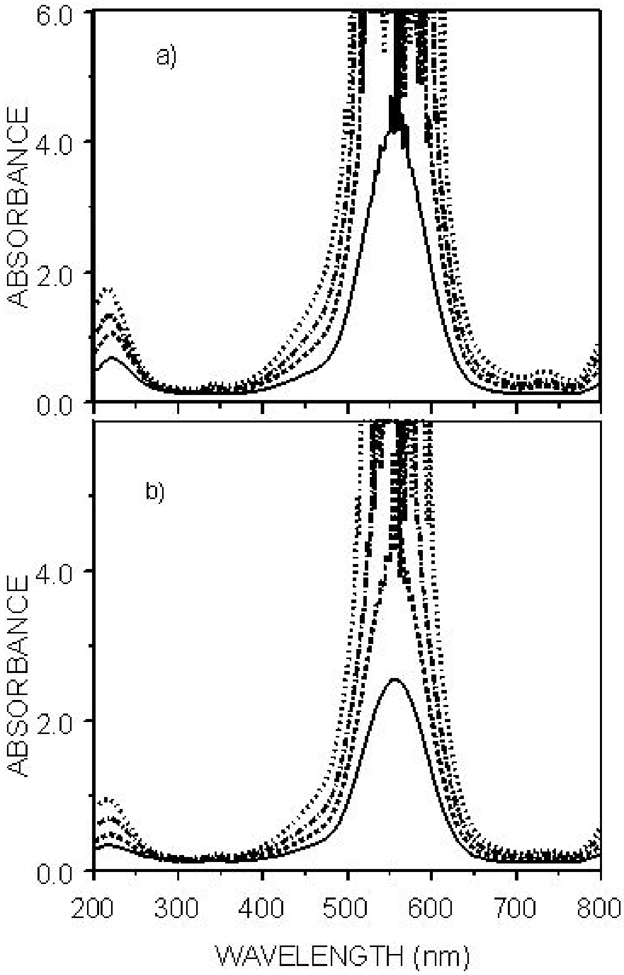

FIGURE 3. Optical absorption of : (a) pure and (b) AC KCl crystals under 1.0 MeV electron irradiation to doses of 100 kGy (solid line), 200 (kGy (broken line), 300 kGy (chain line) and 500 kGy (doted line).

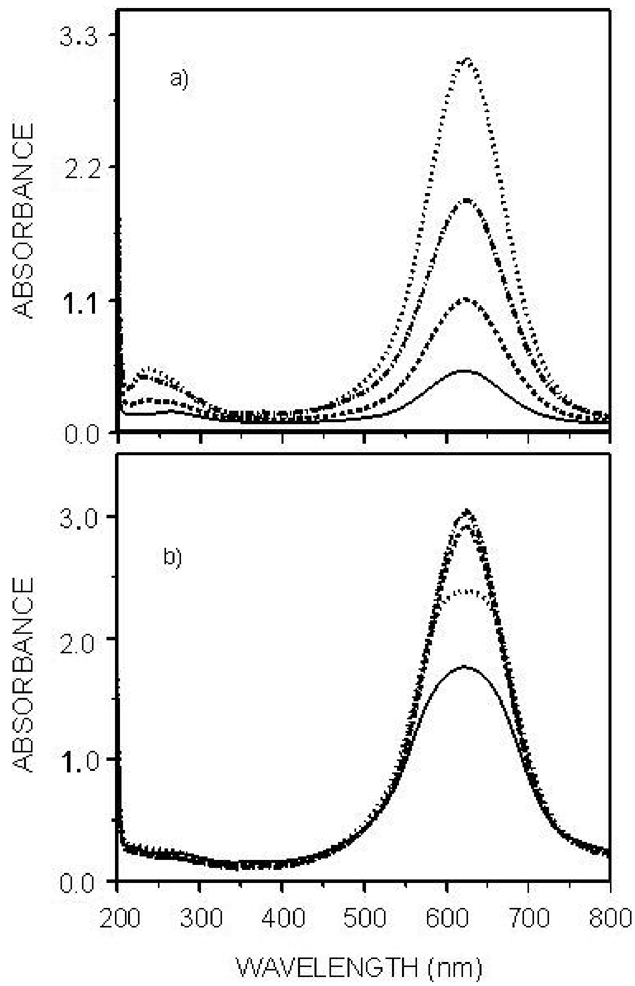

FIGURE 4. Optical absorption of : (a) pure and (b) AC KBr crystals under 1.0 MeV electron irradiation to doses of 100 kGy (solid line), 200 (kGy (broken line), 300 kGy (chain line) and 500 kGy (doted line).

ated pure KBr crystals show the same induced F-center related and UV absorption bands. However, now with the UV bands looking like an envelope of several narrow absorption components. Again, these bands could be related to hole centers previously reported as V bands in the 225-275 nm range in x-irradiated KBr [11]. For all cases, the rise at 200 nm could be associated with the α band [13]. Irradiation with electrons of 1.0 MeV to a dose of 100 kGy induce a very similar behavior for the AC and pure KCl and KBr crystals.

The cumulative dose effect on the absorption spectra for pure and AC KCl and KBr crystals irradiated with 1.0 MeV electrons are shown on Figs. 3 and 4, respectively. In pure KCl and KBr as well as in AC KCl crystals, the absorption spectra show a monotonous increase of the bands but with different growing rates. The effect is more pronounced in pure KBr (Fig. 4a) where the band peaked at 222 nm increases faster than the band at 275 nm. On the other side, in AC KBr samples the irradiation effects are fully different. Few or no effects are observed in the UV bands but a very pronounced effect is seen in the F-center related absorption band. For 100 and 500 KGy, the F band looks like two overlapped bands but for 200 and 300 KGy the typical F center absorption band is recovered. In addition, the intensity of the F band shows a saturation that will be discussed in the next section.

4. Discussion

As it is well known, electron irradiation on AH mainly produces Frankel pairs like F and H centers. The decreasing of the F_2^+ and F_2 bands suggest that the H centers produced by the electron beam recombine with one of the electrons from preexisting F_2^+ and F_2 centers. That recombination increases the F center concentration and almost bleaches the F_2 center concentration. The weak F_2-related absorption band remains after bleaching because the clustering of F centers due to the high concentration of F centers after irradiation. The halogen bare vacancy left behind after the H-F_2^+ center recombination may form some hole center related with the UV absorption bands as discussed later. These processes are possible

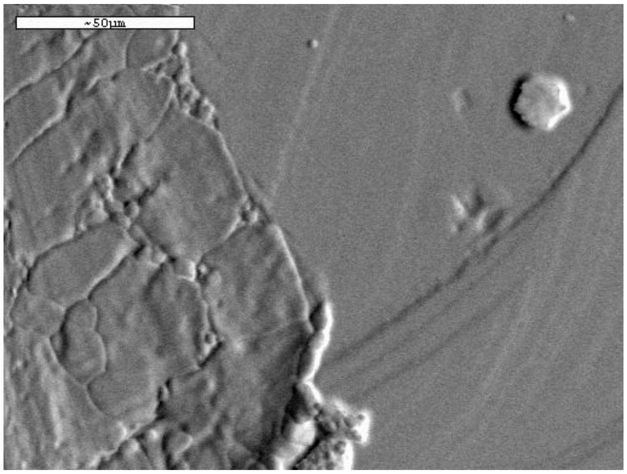

FIGURE 5. SEM image of additively colored KBr crystals after electron irradiation to 1.0 MeV and 100 kGy dose.

because of the high mobility of the H center for temperatures above about 40 K [14]. In addition with the H-F_2^+ and H-F_2 recombination, for high radiation doses H centers can also transform into less mobile clusters of halogen centers like the Cl_n^{m-} molecular and ionic centers (n=1,2,3 and m=1,2) in KCl which are associated with the V absorption bands at RT [15,16]. From dichroism studies of V bands, Winter *et al.* [11] had ascribe the absorption bands at 215 and 222 nm to V_3 centers in KCl and KBr, respectively. Several other V bands have been reported in AH under different experimental condition. For example, in KBr x-irradiated at 100K an absorption band at 275 nm has been related with a V_4 defect and in KCl the bands at 240 and 230 nm with V_4 and V_2 centers at 100 and 200K, respectively [11]. In KCl the small shift to lower wavelengths at larger cumulative doses (Fig. 4) can be explained because above 250K some V_2 centers are converted to V_3 [11]. The present results confirm the intrinsic holes formation (V and H centers) in KBr and KCl by high-energy electron irradiation and suggest these several defects are dependent on doses as well as irradiation temperature like in Refs. 11 and 17.

Another effect of electron irradiation of AH is the efficient desorption of alkali and halogen atoms from the surface due to the F and H centers diffusion from the bulk and their interaction with the surface. The trapping of the F center at the surface requires that the F center is mobile, which is not the case at room temperature. However, the efficient desorption process in electron irradiated AH is explained assuming that the F center just after its creation is in an excited state (F*) which is mobile [4,7,18]. The diffusing F* center is stabilized producing a stable F center close to the surface, within the F* diffusion length and the surface topography [8]. Further, it is seen that the position of the F band in irradiated KCl and AC KCl is similar suggesting that most of the original F centers in AC KCl have been destroyed by the F-H recombination during the irradiation. The shift of the related F-center absorption band in irradiated KCl could be due to the formation of trapped F centers at surface imperfections. Assigning the red shift to a surface F center is plausible because like in a hydrogenic model, the $1s$ ground state change continuously to $2p_z$ state when the positive charge (halogen vacancy in our case) is moved from well inside of the bulk to the surface as in the case of Wannier excitons near a semiconductor surface[19].

On the other hand, desorption fluxes of K and Na atoms have been observed in KBr and NaCl irradiated with electrons of 1.0 keV for several temperatures [7,8]. In agreement with the alkali atom desorption process, this means that some F* centers are annihilated in the surface and a fraction of them are reflected back to the bulk where they are stabilized as F centers. Accordingly, in the case of pure and AC irradiated KBr the peak position of the F center related absorption band does not change by irradiation (Fig. 2). The intensity saturation and broad shape showed by the absorption band of AC KBr under cumulative dose (Fig. 4) could relate with the surface state. As was mentioned, desorption is controlled by the surface topography and results in Refs. 7 and 8 were obtained on surfaces very clean and well ordered. In our case, SEM images (Fig. 5) show a surface with some regions formed by grains of several sizes and shapes that can account for the production of a distribution of reflected F* centers that can stabilize from the surface to the bulk giving a broad shape for the F band. However, this is no conclusive and additional measurements are now in progress. On another hand, it is important to stress the different behavior of V absorption bands related with hole centers (H centers aggregates) in pure and AC KBr under electron irradiation (Figs. 2 and 4). In irradiated pure crystals the V bands are clearly observed but they are absent in irradiated AC samples. Due to the main channels for recombination of H centers in AC KBr are the pre-existing and the irradiation induced F centers in addition to desorption of Br ions via H centers[7,8], the density of H centers produced by irradiation could be not enough to form aggregates of H centers. In contrast, in pure KBr there are not pre-existing F centers and this recombination channel for H centers is not active one.

5. Summary

We have found that high energy electrons bombardment on KCl and KBr crystals induced several optical effects. In additively colored KCl the irradiation destroys the F_2^+ centers and strongly diminish the F_2 defects. At the same time, the F centers related absorption band increase and the band position shifted to low energy. The band peaked at 558 nm is assigned to superficial F centers. In KCl, superficial F centers and F-center aggregates (type F_2 centers, deep in bulk) as well as different H center aggregates (V bands) are the main defect production. In KBr crystals the pre-existing F centers anneal the V bands and there is no evidence of superficial F centers formation. All results are consistent with alkali and halogen atoms desorption and H-F recombination processes.

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