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Room-Temperature Colorability of Alkali-Doped KBr

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The results reported in this paper show that lithium impurities stabilize interstitial halogen atoms also at 300 °K in the form of *V*(306) centers. The number of stabilized interstitials is limited by the diffusion of anion vacancies and their recombination with the interstitials. As a consequence, lithium impurities introduce a rapidly saturating first stage in the *F*-center growth curve.

I. INTRODUCTION

It is now well established that the radiation damage in alkali halide crystals consists of anion vacancies and interstitial halogens. Radiation-produced vacancies and interstitials may be variously charged and may be found either isolated or bound to lattice defects or, finally, in the form of aggregates. The type and the amount of defects produced depend on the energy and intensity of radiation, on the degree of perfection of the sample, and on the irradiation temperature. The irradiation temperature plays a major role when it is sufficiently high to allow the diffusion of interstitials and/or of vacancies. In this case, back reactions, i.e., mutual annihilation of vacancies and interstitials, clustering processes, and trapping of vacancies and interstitials by lattice defects, greatly influence the radiation-damage process.[1]

In previous papers, the influence of alkali impurities as interstitial traps on the color-center production has been studied in the liquid-nitrogen temperature (LNT) range.[2–4] In this paper we extend the investigation to the room-temperature (RT) range where interstitial trapping is greatly reduced[4] and where anion-vacancy diffusion (which is inhibited at LNT) may play a role.

II. EXPERIMENTAL

The color-center production in pure or lithium-doped KBr has been studied by inspecting the growth of the optical-absorption bands associated with the color centers. During the x irradiations (performed with an OEG-50T Machlett tube operated at 45-kV peak and at 30 mA) and the subsequent optical-absorption measurements, the temperature of the sample holder was automatically maintained within ± 0.3 °K of the reported temperature.

The dichroic absorption spectra reported in this paper have been obtained with a HNP'B Polaroid filter inserted in the light beam of a Hitachi EPS 3T double-beam spectrophotometer. The filter was put in a position of the optical path where the beam was not yet split, just in front of the sample. The same filter, as well as the standard uv source of the spectrophotometer, have been used for the preferential bleaching of color centers with polarized light.

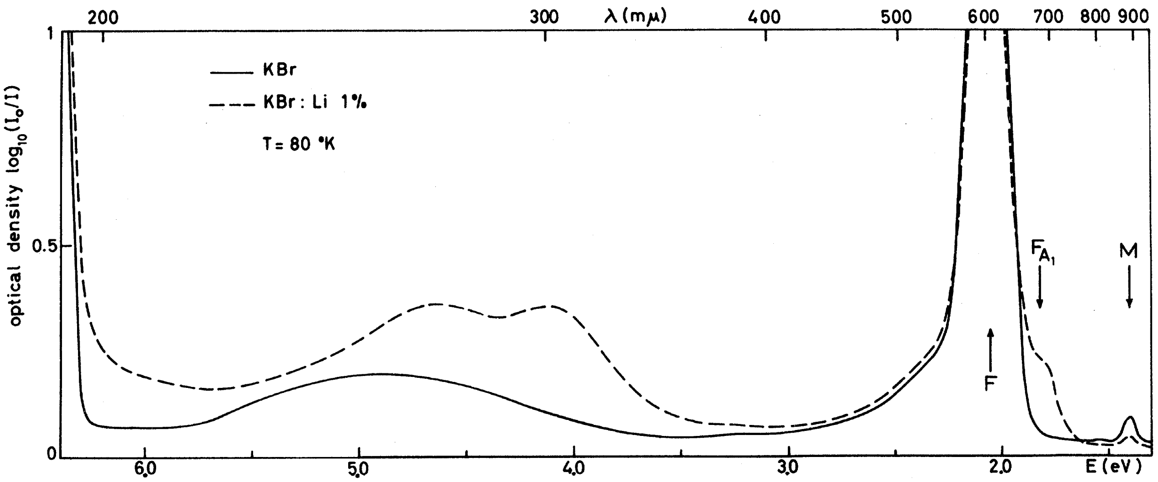

FIG. 1. Absorption spectra of two samples x irradiated at 300 °K for 5 h. These spectra have been obtained by subtracting those obtained prior to the x irradiation from the measured absorption spectra.

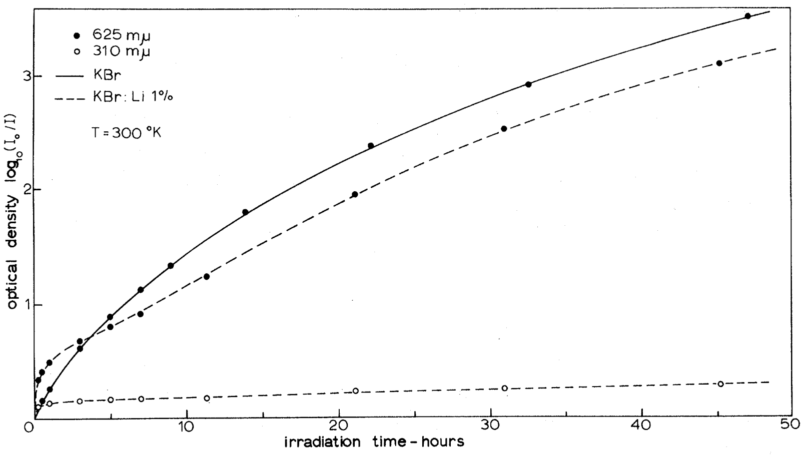

FIG. 2. Growth curves of the F band (625 mμ) and of the $V(306)$ (310mμ) band. No corrections have been made for the contribution to the absorption of the F_A and M bands in the region of the F band. The apparent slow growth of the $V(306)$ band which follows the initial steep rise is due to the growth of the V_2 band which overlaps the $V(306)$ band. Sample thickness: KBr $= 0.71$ mm; KBr : Li $= 0.73$ mm.

The samples used have been grown in nitrogen atmosphere by the Kyropoulos method. The reported amounts of impurities always refer to the quantities added to the starting KBr powder (Merck Suprapur).

III. RESULTS AND DISCUSSIONS

An inspection of the absorption spectra after short irradiations (Fig. 1) shows that lithium-doped KBr exhibits, along with the absorption bands of pure KBr, a band with an apparent peak at 304 mμ (at 80 °K) and the F_{A_1} (Li) band. Owing to the overlapping of the F and F_A bands, the growth curve of Fig. 2 concerning the lithium-doped sample gives information on the total number of vacancies produced (F and F_A centers).

Lithium impurities enhance the anion-vacancy production at 300 °K for short irradiations (Fig. 2). For longer irradiations the anion-vacancy production is independent of the impurity content of the sample, as is shown by the fact that the slope of the growth curves is the same for pure and lithium-doped samples (Fig. 2). In lithium-doped KBr, the average anion-vacancy production efficiency is about five times larger in the first 15 min than in the subsequent 15 min. As is shown in Fig. 3 the F- and F_A-center production efficiency remain in a constant ratio at least for the first 5 h of irradiation.[5] Therefore, the decrease of the anion-vacancy production efficiency which occurs at shorter irradiations cannot be explained in terms of a decreasing production efficiency of F_A centers. The initial high production efficiency of F centers and its subsequent decrease must instead be correlated with the growth and saturation of the band whose apparent peak is at 304 mμ (Figs. 1 and 2).

It has been shown that two bands peak at 306 mμ (near LNT) in x-irradiated KBr: the so-called V_7 and V (306) bands. V_7 centers are formed at RT and have a ⟨110⟩ symmetry axis; V (306) centers are produced below 240 °K and have a ⟨100⟩ symmetry axis.[6] The band produced at 300 °K in lithium-doped KBr presents at ⟨100⟩ dichroism when bleached with light polarized in a ⟨100⟩ direction (Fig. 5). On the other hand, no dichroism can be induced in this band when the bleaching light is polarized in a ⟨110⟩ direction. This behavior is typical of a band arising from centers with ⟨100⟩ symmetry axis. Furthermore, the half-width of the band produced at 300 °K in lithium-doped KBr is the same as that of the V (306) band. We are then led to the conclusion that V (306) centers are produced also at 300 °K, provided that the sample contains lithium impurities.

On the basis of the fact that V (306) centers have properties similar to those of the V_4 centers (di-

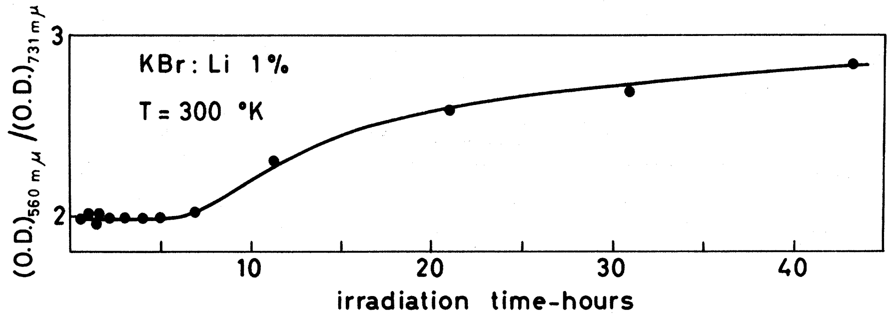

Fig. 3. Ratio between the optical densities at 560 and 731 mμ as a function of the irradiation time. This ratio gives information on the relative production of F and F_A centers.

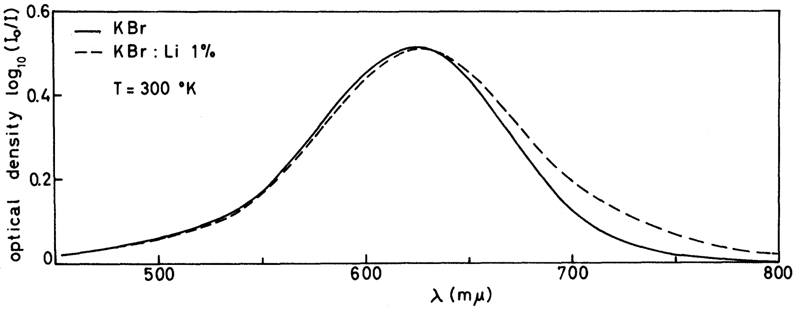

FIG. 4. Absorption spectra of a pure and a lithium-doped KBr sample showing that the ratio reported in Fig. 3 is a reliable measure of the relative production of F and F_A centers. The pure sample has been irradiated for 2 h, the lithium-doped sample for 1 h.

interstitial centers) and that their production is enhanced by sodium and lithium impurities, Saidoh and Itoh suggested that the V (306) band arises from a particular configuration of the V_4 center not stable in pure crystals and stabilized by suitable alkali impurities.[7] This hypothesis is also supported by the fact that the thermal stability of V (306) centers is higher in lithium-doped KBr than in nominally pure KBr [where no V (306) center can be found above 240 °K[6]]. In this framework, the V (306) centers observed in nominally pure KBr should be due to trace impurities of sodium and their lesser thermal stability [with respect to that of V (306)-Li centers] should be due to the larger size of sodium impurities.[4,7] From the above considerations we can conclude that lithium impurities trap and stabilize interstitial halogens also at 300 °K in the form of V (306) centers.

We are now in a position to try to explain the shape of the growth curve of Fig. 2 concerning lithium-doped KBr. Three points must be taken into account: (a) V (306) centers are interstitial centers associated with lithium impurities; (b) the saturation of the V (306) band growth is not due to the exhaustion of lithium impurities, as is proved by the fact that F_A (Li) centers keep being produced after the saturation of the V (306) band; (c) anion vacancies are mobile at 300 °K.[4]

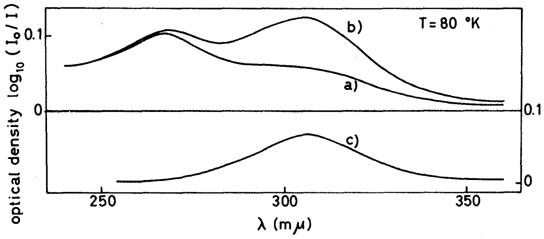

FIG. 5. Dichroic behavior of the band peaking at 304 mμ in KBr : Li. (a) Absorption spectrum measured with light traveling along the [$\bar{1}$00] direction and polarized in the [001] direction, after bleaching with light polarized in the same direction; (b) absorption spectrum measured with light polarized in the [010] direction; (c) difference between (b) and (a). Bleaching light data: λ = 306 mμ; slit width = 1 mm; illumination time, 48 h.

At low x-ray doses, lithium impurities enhance the F- (and F_A-) center production by stabilizing interstitial halogen atoms in the form of V (306) centers. However, owing to the migration of anion vacancies, lithium impurities also act as recombination centers between the trapped interstitials and the anion vacancies. In this way a stationary concentration of V (306) centers is built up; thereafter the F-center production efficiency reduces to that of pure KBr. If this interpretation is correct, the production of V (306) centers will depend on the anion-vacancy mobility and, consequently, on the temperature of the sample. We have found that at 80 °K, where the anion-vacancy diffusion is inhibited, the V (306) growth curve does not show any saturation even after 6 h of irradiation and at a concentration of V (306) centers about two times larger than that obtainable at 300 °K. An extension of our investigation to intermediate temperatures and to various radiation intensities is planned. The use of different radiation intensities is suggested by the fact that forward and back reactions in color-center production do not generally have the same dependence on radiation intensity, thereby introducing an intensity dependence of the stationary conditions.[8]

IV. CONCLUSIONS

The data reported in this paper lead to the following conclusions: (i) Lithium impurities introduce a rapidly saturating first stage in the F-center growth curve of KBr at 300 °K; (ii) the enhancement of the F-center production in the first stage is due to interstitial trapping and stabilization by lithium impurities; (iii) the saturation of the first stage is the result of a balance between interstitial -trapping and interstitial-vacancy recombination at lithium impurities.

ACKNOWLEDGMENTS

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[1] See, for example, J. H. Crawford, Jr., Advan. Phys. 17, 93 (1968).

[2] G. Giuliani, Nuovo Cimento 58B, 366 (1968).

[3] G. Giuliani, Solid State Commun. 7, 79 (1969).

[4] G. Giuliani, Phys. Rev. B 2, 464 (1970).

[5] In this figure the ratio between the optical densities at 560 and 731 mμ is reported as a function of the irradiation time. The fact that this ratio is a convenient measure of the relative production of F and F_A centers is shown in Fig. 4.

[6] T. Ishii, J. Phys. Soc. Japan 21, 2202 (1966).

[7] M. Saidoh and N. Itoh, J. Phys. Soc. Japan 29, 156 (1970).

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