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Deformation-induced nonradiative decay of color centers in alkali halides

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It is shown that the coloration of the microcrystalline powders of KCl, KBr, and KI is completely lost within 24 h when the colored powders are stored in dark, at room temperature, whereas the single crystals of these materials subjected to the same treatment can retain the coloration for at least several years. The decay of color centers is through nonradiative modes. The presence of alkali and halogen impurities greatly influences the decay in the powders. It is suggested that the decay involves dislocation motion and such experiments can give important information about defect interactions.

I. INTRODUCTION

It is known that stable color centers can be formed in the alkali-halide crystals using various methods.[1] The concentration of the color centers in the alkali-halide crystals which have been exposed to the ionizing radiations initially decreases after the coloration is stopped owing to recombination of some of the centers, and then reaches a constant value.[2-4] The colored crystals can be stored at room temperature, in dark, without any loss of coloration for a period of several years.[2] In the polycrystalline pellets and in the microcrystalline powders, on the other hand, the color centers bleach much more rapidly.[5-8] It was thought that this is due to the enhanced recombination in polycrystallites.[5] Recently, we have shown that even the colored microcrystalline powders obtained by crushing the electrolytically colored single crystals show this rapid isothermal bleaching, when the powders are stored in dark at room temperature.[9-11] Since in the electrolytic coloration only one type (excess electron) of centers was formed, the decay of color centers is not due to recombination but through some nonradiative mode. It has further been shown that the rate at which the isothermal decay of color centers, in the microcrystalline powders when the powders are stored in dark at room temperature, proceeds is not the same for all the powders. The rate decreases as one moves from Li^+ to Rb^+ and from F^- to I^- along the alkali-halide series. Thus, the microcrystalline powders of NaF, NaCl could be stored in dark without any appreciable loss of coloration for several months, but the powders of KCl, KBr lost all their coloration within 24 h and that of RbI within a couple of hours. Since such a nonradiative destruction of color centers is not observed in the single crystals, the processes responsible for it must originate within the defects inherent to the microcrystalline state. Thus, the microcrystalline powders can be thought as made up of two, physically interwined subsystems. One, the perfect-lattice subsystems, the perfect lattice being preserved due to cleavage properties, and another, the imperfections (made up of dislocations, etc.) which bind the small indestructible regions within each crystallite (Hersh, private communication). The rapid isothermal decay of color centers observed in the microcrystalline powders may originate within the interaction between these two subsystems. The study of this decay, in turn, may give important information regarding these defect interactions. In the present paper, the results on the stability of color centers are described for several alkali-halide crystals.

II. EXPERIMENTAL

The single crystals of KCl, KBr, KI, pure and doped with alkali-metal and halogen impurities, were grown in the laboratory from the melt. G.R. grade powders were used as starting materials. Mixed crystals of various compositions, KCl-KBr and KBr-KI, were also prepared by the same method. The nearest-neighbor distance in the mixed crystals was measured by taking x-ray diffraction photographs which also ensured the formation of the mixed crystals. The single crystals of approximate size $15 \times 5 \times 5$ mm^3 were cleaved from the as-grown blocks and colored electrolytically. The details of the electrolytic coloration are described elsewhere.[12] KCl, KBr, and KCl-KBr crystals were colored by x rays (30 kV, 10 mA) also. A 1–1.5-mm-thick slice was cleaved from the central portion of the colored crystal for the optical-absorption measurements and the remaining crystal was then crushed to fine powder (40–60 mesh). The absorption measurements on the single crystals were carried out with a Carl Zeiss spectrophotometer VSU 2P. The coloration in the crushed powders was studied by measuring the diffused reflectance as a function of

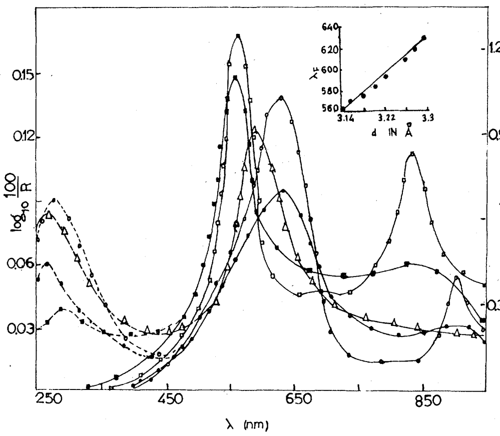

FIG. 1. Optical spectra of different colored specimens. □, KCl single crystal; ○, KBr single crystal; ■, KCl microcrystalline powder; ●, KBr powder; △, KCl-KBr powder. The dashed curves show the absorption band in the uv observed in x-rayed samples. The $\log_{10}(100/R)$ scale is for reflectance spectra of powders and the absorption-coefficient $\alpha(\text{cm}^{-1})$ scale for the optical-absorption spectra of the single crystals. The inset shows the variation of the F-center absorption maxima with nearest-neighbor distance.

wavelength. The reflectance measurements were made on the same spectrophotometer using a 45/0 reflectance attachment.

III. RESULTS

The results of the optical absorption measurements for KCl, KBr, and KCl-KBr are presented in Fig. 1. Five compositions of KCl-KBr, viz., 5 : 1, 3 : 1, 1 : 1, 1 : 3, and 1 : 5 were studied. The coloration of the single crystals is not different from that described in the literature. In electrolytically colored crystals, a prominent F band appears at 560 nm in KCl and at 630 nm in KBr. On the long-wavelength side of the F band, the F_2 band appears at 830 nm in KCl and 920 nm in KBr. In the mixed single crystals KCl-KBr the position of the F-center absorption maxima depends upon composition. The variation of the F-center absorption maxima with the nearest-neighbor distance d is shown in the inset of Fig. 1. The reflectance curves of the colored powders are also shown in Fig. 1. The details of the reflectance spectra of the microcrystalline powders can be found elsewhere.[7,9,13] The F and M bands are seen in the powders also. In the samples colored by x rays, an additional band is observed in the uv region which is due to trihalogen absorption.

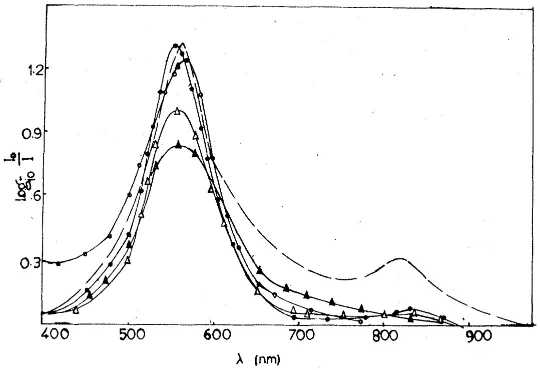

FIG. 3. Optical absorption spectra of electrolytically colored single crystals of KCl doped with alkali and halogen Impurities. Dashed line, KCl-F; ○, KCl-I; ●, KCl-Li; △, KCl-Rb; ▲, KCl-Cs. Alkali impurity, 1 mol%; halogen impurity, 1.5 mol%.

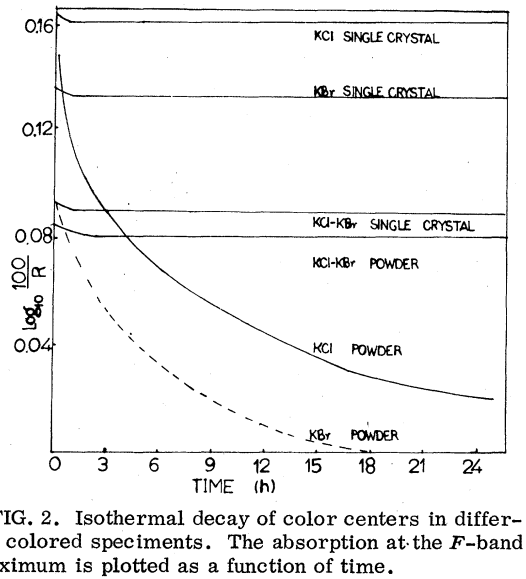

FIG. 2. Isothermal decay of color centers in different colored speciments. The absorption at the F-band maximum is plotted as a function of time.

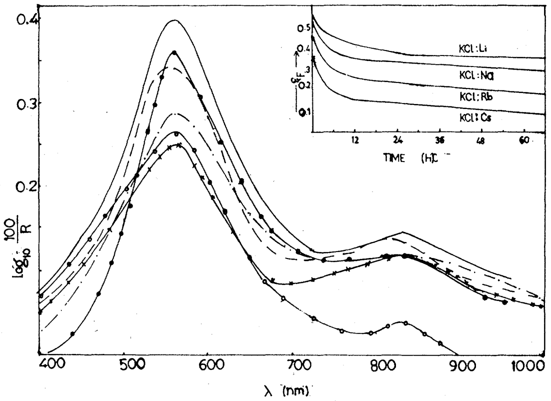

FIG. 4. Reflectance spectra of the powders obtained by crushing the electrolytically colored crystals of KCl doped with alkali and halogen impurities. ○, KCl-F; ×, KCl-I; dash-dot line, KCl-Na; ●, KCl-Cs; dashed line, KCl-Li, and solid line, KCl-Rb. The inset shows the variation of the absorption at the F-band maximum with time.

Important for the present paper is the isothermal decay of color centers when the colored specimens are stored in the dark at room temperature. This is shown in Fig. 2. The single crystals of KCl-KBr, KCl, and KBr can retain the coloration for, at least several months without showing any aging effect. The coloration of the microcrystalline powders of KCl and KBr, on the other hand, is lost within 24 h. The decay is uniform over the entire spectral range. Thus, this is different from the optical or thermal "bleaching" of the color centers in which some of the centers are transformed to form *F* aggregate centers. The powders colored by x rays and those obtained by crushing the electrolytically colored single crystals show similar decay. The decay was found to be independent of dose and initial color-center concentration. The decay is not due to recombination. It was observed that electrolytically colored powders were not thermoluminescent. In view of this fast decay of the coloration of the microcrystalline powders of KCl and KBr, the stability of the coloration of KCl-KBr powders is suprising and rather inexplicable. Considering these results, the role of the impurities in preventing the nonradiative destruction of color centers seems important, and similar experiments were performed on crystals doped with other halogen and alkali-metal impurities.

Figure 3 shows the absorption spectra of the single crystals of KCl-Li, KCl-Na, KCl-Rb, KCl-Cs, KCl-F, and KCl-I. The impurity concentration is 1 mol% for cation-doped crystals and 1.5 mol% for anion-doped crystals. All the crystals show an *F* band around 560 nm. The reflectance spectra of the powders obtained by crushing these crystals are shown in Fig. 4. In the inset of Fig. 4, the absorption represented by $\xi = \log_{10}(100/R)$, where R is the reflectance, is plotted as a function of time. It is seen that the fast decay observed in pure KCl is profoundly reduced in the doped powders. The decay of color centers is observed for some time, and then a stable value of color-center concentration is attained. The coloration then can be retained for at least several months without any aging effect when the powders are stored in the dark at room temperature. The period during which decay is observed is reduced as the misfit between host ion (K^+) and impurity ion increases. In KCl-Cs, however, decay proceeds faster. This is perhaps due to the precipitation of Cs. In the halogen-doped impurities it is observed that the stability of the coloration increases with the increasing misfit between host (Cl^-) and impurity ions.

To examine whether the stabilization of the color centers in microcrystalline powders is observed in the other alkali halides also, similar experiments were performed on KBr and KI. The optical absorption of KBr-Cs, KBr-Na, and KBr-Rb containing impurity alkali-metal ions in 5 mol%, and of various compositions of KBr-KI is shown in Fig. 5. Some samples of KBr-Na and KBr-Cs containing 10 mol% of Na or Cs were also studied, but these systems slowly decomposed. These crystals assumed a foggy appearance after 24 h. For the KBr-KI system five compositions 5 : 1, 3 : 1, 1 :1, and 1 : 5 were prepared. Only the

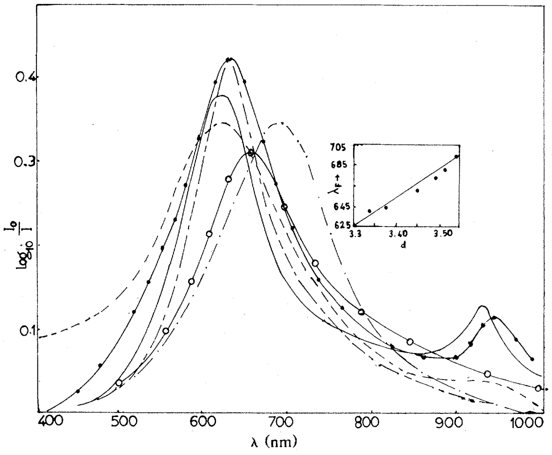

FIG. 5. Optical-absorption spectra of the single crystals of KBr-KI and KBr doped with alkali impurities. Solid line, KBr; dash-dot line, KI; ○, KBr-KI; ———, KBr-Rb; ●, KBr-Cs; dashed line, KBr-Na. The inset shows the variation of the *F*-band absorption maxima with the nearest-neighbor distance for the KBr-KI system.

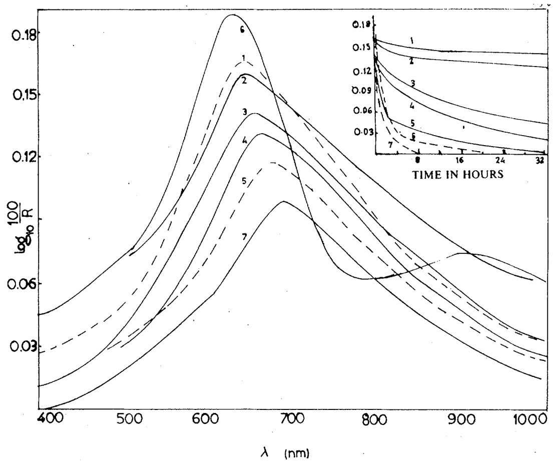

FIG. 6. Reflectance spectra of the powders of KBr-KI obtained by crushing the electrolytically colored single crystals. KBr-KI compositions: 1, 5:1; 2, 3:1; 3, 1:1; 4, 1:3; 5, 1:5; 6, pure KBr; 7, pure KI. The inset shows absorption at the *F*-band maximum as a function of time.

equimolar composition was found unstable; it decomposed within a couple of days. The other crystals could be stored in a dry place for several months. For alkali-doped KBr, the *F* band is observed around 630 nm. In KBr-KI, the position of the *F*-center absorption maxima depends upon composition. The variation of the *F*-center absorption maxima with nearest-neighbor distance is plotted in the inset of Fig. 5. The reflectance curves of the microcrystalline powders obtained by crushing the electrolytically colored crystals of KBr-KI are shown in Fig. 6. The decay of the coloration with time is shown in the inset of Fig. 6. It is seen that for all the compositions, microcrystalline powders of KBr-KI are more stable than the powders of pure KBr and KI. The decay reduces with increasing percentage of KBr. The KBr-KI composition 5 : 1 was found most stable and these powders could retain the coloration for a few days. Similar results for alkali-doped KBr powders are shown in Fig. 7. Again, it is seen that the decay observed in pure KBr is profoundly reduced by the addition of alkali-ion impurity. The effect of impurity increases with the increasing misfit between the host and impurity ions. Thus the decay is markedly reduced in KBr-Cs, but not so in KBr-Rb.

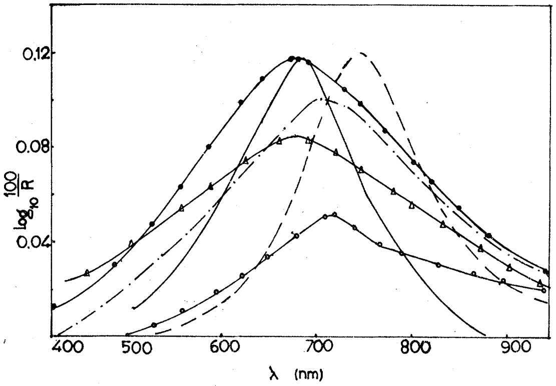

FIG. 8. Reflectance spectra of the powders obtained by crushing the electrolytically colored single crystals of KI doped with various impurities. △, KI; dashed line, RbI; dash-dot line, KI:Rb; ●, KI:Na; solid line, KI-Cl; ○, KI:Cs.

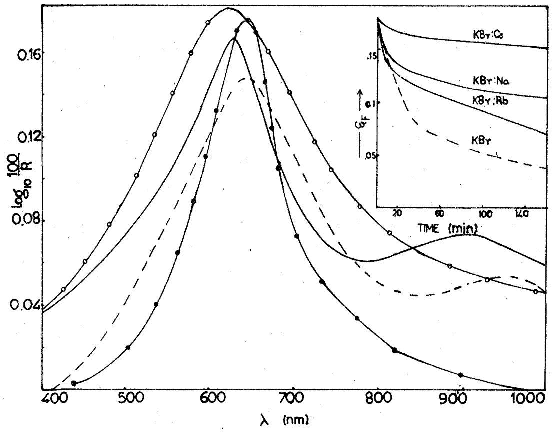

FIG. 7. Reflectance spectra of powders obtained by crushing electrolytically colored single crystals of KBr doped with alkali impurities. Solid line, pure KBr; dashed line, KBr-Cs; ○, KBr-Na; ●, KBr-Rb.

Figure 8 shows the reflectance spectra of the microcrystalline powders of KI, RbI, $K_{0.9}Rb_{0.1}I$, $K_{0.9}Na_{0.1}I$, $K_{0.9}Cs_{0.1}I$, and $KI_{0.985}Cl_{0.015}$. The isothermal decay curves are shown in Fig. 9 which also summarizes the similar data for other cyrstals. The decay is reduced to some extent after the addition of impurities. The effect is marked for KI-Na. These powders can retain the coloration for a couple of days. In Kl-Rb, all of the coloration is lost within 12 h, as compared to 8 h required for the same decay in pure KI and 2 h in pure RbI. In KI-Cs the decay is not reduced. In fact, one would have expected an enhanced effect in Kl-Cs over that in KI-Na. The reason for the ineffectiveness of Cs is that the system KI-Cs is unstable. The single crystals of KI-Cs appear foggy after 24 h. In the reflectance curves also, two overlapping peaks corresponding to the *F* band of KI and CsI can be seen. Thus with the increasing decomposition the decay of color centers proceeds according to the rates observed in the individual crystals. Nevertheless, it is seen that the effect of impurities on the decay rates is not as profound in KI as it is in KCl or KBr. The amount of impurity to be added to observe the effect is about 10 mol%, whereas in KCl even 1 mol% of

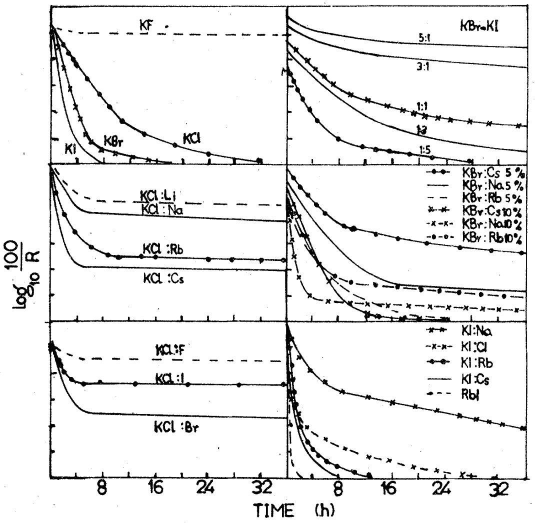

FIG. 9. Isothermal decay curves for various microcrystalline powders.

impurity is sufficient to cause changes in decay rates.

IV. ANALYSIS OF THE ISOTHERMAL DECAY CURVES

The isothermal decay curves can be analyzed by standard methods[3,4] to yield rate constants, half-life, etc. Thus, the color-center concentration I decreases with time and can be represented by an equation of the type

$$I = I_0 e^{-\lambda t} ,$$

where λ is known as the rate constant and is given by the slope of the graph between $\ln I$ and t. This is true if the process is governed by only one rate constant. In general, I is given by

$$I = \sum_j I_j e^{-\lambda_j t} ,$$

and the different rate constants can be obtained by evaluating the slopes of the graph between $\ln I$ and t in different regions. These are listed for different crystals in Table I. It is observed that even for pure powders two rate constants are observed. In doped samples, the initial decay is governed by the rate constants observed in pure salts, and a stable component is seen thereafter. Thus, in all the doped crystals (in microcrystalline powder form) of KCl, two center groups can be visualized: one which decays continuously and can be identified with the similar centers in pure powder, and another which is completely stable. The dominance of the stable component varies with dopants. In KCl-Li the decay is observed only up to 2 h, in KCl-Na up to 4 h, and in KCl-Rb up to 8 h. Thus the rate constants are almost the same in these samples but the initial concentration of the decaying centers decreases with the increasing misfit between host and impurity ions. In KCl-Cs, however, a greater value of rate constant is observed. This most probably is due to the slow decomposition of the system and is not a true decay characteristic of the mixed powders. The conclusions drawn from the results on cation-doped KCl are born out by the similar results obtained for anion-doped samples. In KBr, the impurities play a less dominant role, the rate constants after addition of impurities do not show a definite trend, but qualitatively, a similar dependence on the misfit between host and impurity ions is observed. The effect of impurity addition is least prominent in KI. Thus, it is seen that inhibition of the nonradiative isothermal decay of color centers in the microcrystalline powders of alkali halides in a general phenomenon. The effect is observed prominently in KCl and it decreases in KBr and KI, in the given order. The effect is most prominent for the impurities for which the misfit between host and impurity ion is greatest.

TABLE I. Rate constants for the nonradiative isothermal decay of color centers in different microcrystalline powders.

System	Rate constants λ_1 (10^{-4} sec^{-1})	λ_2 (10^{-5} sec^{-1})
KCl	0.2208	0.696
KCl-Li	0.220	
KCl-Na	0.265	
KCl-Rb	0.26	
KCl-Cs	0.662	
KCl-F	0.2208	
KCl-I	0.236	
KCl-Br	0.301	
KBr	0.41	0.690
KBr-Rb	0.47	
KBr-Na	0.22	
KBr-Cs	0.207	
KI	0.66	2.09
KI-Na	0.414	0.024
KI-Rb	0.395	
KI-Cl	0.94	0.69
KI-Cs	1.10	

The next important parameter is the activation energy for the process of nonradiative destruction of the color centers. It is related to the rate constant λ, through the relation

$$\lambda = \lambda_0 e^{-E/kT} .$$

Thus, E can be obtained from the slope of the graph between $\ln\lambda$ and $1/T$. It is difficult to study the temperature dependence of the rate constant, because the decay proceeds much faster with increasing temperature, and only a limited temperature range (0–50 °C) is available for the observations. For this reason, the temperature dependence of the rate constant and the activation energy can not be determined accurately. We estimate E to be of the order of 0.18 eV for KCl and 0.15 eV for KBr.

V. DISCUSSION

The reason for nonradiative destruction of color centers in microcrystalline powders is, as yet, not clear. As the decay is observed only in powders and not in single crystals, the processes responsible for it must originate within the defects inherent to the microcrystalline state. The microcrystalline state is characterized by a high density of lines and planar defects and other grosser imperfections. Microcrystalline powders can be considered as extremely deformed single crystals and high dislocation densities are to be expected. It may happen that F-center electrons may be annihilated in a charged dislocation. The charged dislocations are known to exist at room temperature. The clusters of vacancies are responsible for the charge on the dislocations.[13,14] Further, the activation energy for charge transport by dislocation motion is of the order of 0.12 eV.[15] The estimated value of the activation energy for the destruction of color centers in microcrystalline powders is also of the same order. Another possibility is that F-center electrons may form some complex defect with association of dislocations and other imperfections. The complex defect may show optical absorption in an entirely different wavelength range. Thus, F electrons may be rendered optically unobservable without actual annihilation. The modification of the decay by the addition of impurities is still more difficult to conceive. The reported observations remind one of experiments related to F-center production in the mixed alkali-halide single crystals.[16] It was found that the coloration efficiency in the mixed crystals decreases owing to disruption of the collision sequence along $\langle 110 \rangle$ by the foreign ion in that direction. It may be that the isothermal decay observed in microcrystalline powders involves a certain sequence and the sequence may be disrupted by the presence of the impurity.

At present, only these speculations can be offered for the explanation of the phenomenon. A series of experiments will be required to arrive at its origin. However, it is certain that these experiments will be of great help in understanding the defect interactions, the motion of the charged dislocations, etc.

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