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Optical, Electrical, and ESR Studies of Additively Colored KCl Doped with Magnesium

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The plots of $\log_{10}\sigma T$ as a function of $1/T$ for the uncolored crystals of KCl doped with magnesium show the usual intrinsic and extrinsic regions. The value of the energies derived from the conductivity plot are $W=2.14$ eV for the energy of formation of a separated pair of vacancies, $E=0.75$ eV for the energy of activation for the migration of a cation vacancy, and $W_a=0.42$ eV for the energy of association of a cation vacancy with a Mg^{2+} center. These crystals give an optical absorption band peaking at 272 nm. After additive coloration, magnesium does not introduce any additional bands in the visible or ultraviolet regions of the spectrum. On optical bleaching of the colored crystals at room temperature, the usual F-aggregate bands are formed at the expense of the F band. On heating the colored crystal above 100°C, F centers start decreasing in number and a broad optical absorption band peaking at $\sim$320 nm starts developing. The alkali-metal colloids are not formed in these crystals. The centers responsible for the 320-nm band are unstable above 350°C. The centers responsible for the 272- as well as for the 320-nm bands are not paramagnetic. The conductivity ratio σ_c/σ_n, where σ_c is the conductivity of the colored crystal and σ_n that of an identical uncolored crystal, remains less than unity from 100 to 600°C.

1. INTRODUCTION

THE electrical conductivity of alkali halides doped with Ca, Sr, Ba, Cd, etc. impurities has been studied extensively.[1] Recently, it has been shown that when alkali-halide crystals doped with Zn, Cd, and Hg are colored additively, an intense optical absorption band, in addition to the F band in the visible, is formed in the ultraviolet region of the spectrum.[2–4] The equilibrium concentration of the F centers in Cd-doped crystals is found to decrease and that of the ultraviolet band centers to increase with the increase in the impurity concentration in the crystal.[3,4] It has also been found that in cadmium-doped crystals the F and the ultraviolet bands are resistant to optical bleaching at room temperature. If the colored Cd-doped crystals are exposed to F or visible light or heated to higher temperatures, no Z zenters[5,6] or alkali-metal colloids are produced.[4] Such studies on the KCl crystals doped with magnesium have not been made.[2–6] The optical, ESR, and electrical properties of uncolored and additively colored KCl crystals doped with magnesium have now been studied in detail, and the results are reported in this paper.

2. EXPERIMENTAL

The methods of growing the pure and magnesium-doped KCl crystals, quenching or slowly cooling them, additive coloration, optical or thermal bleaching of the colored crystals, and measuring the optical and ESR absorption and electrical conductivity are the same as discussed earlier.[4,7,8] Crystals were grown from spectrographically pure (obtained from Johnson, Matthey and Co., Ltd., London) and *BDH* analar purity KCl powders and E Merck's grade $MgCl_2$. The letters H, B, and D denote the crystals grown from crystals that are spectroscopically pure, analar pure, and doped with magnesium, respectively. The amount of $MgCl_2$ added to the KCl melt was varied from 0.25 to 2.0 wt%, but the absolute concentration of Mg^{2+} in the crystal was not determined. The concentration of background divalent cation impurities in H and B crystals is, respectively, $\sim$1 and $\sim$10 ppm.[7] The optical and ESR absorption measurements were made at room temperature.

3. EXPERIMENTAL RESULTS

A. Ionic Conductivity

The usual plots of $\log_{10}\sigma T$ versus $1/T$ for the various crystals are shown in Fig. 1. In this figure, curve 1 is for the H crystal and curve 2 is for the B crystal. Curves 3–5 in Fig. 1 are for the three D crystals doped with 0.25, 1.0, and 2.0 wt% of $MgCl_2$ in the melt, respectively. The observed plots can be divided into three different regions,[8] region I which is intrinsic, region II where the concentration of free-cation vacancies is equal to the divalent cations present in the crystal, and region III where the association of cation vacancy and the divalent cation becomes important. It is seen that in the high-temperature region I, all observed points plot on a single straight line with the slope $\frac{1}{2}W+E=1.82\pm0.05$ eV, where W is the energy of formation of

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a separated pair of vacancies and E is the energy of activation for the migration of a cation vacancy. At temperatures below the intrinsic range, the parallel straight-line plots of region II are shown extended by the broken straight lines. The slopes of the plots in regions II and I give $E=0.75\pm0.05$ eV and $W=2.14\pm0.1$ eV, in agreement with the earlier values.[1,8]

At lower temperatures, some of the cation vacancies and the impurity ions form pairs and the conductivity plots bend downwards, giving region III.[1,8] Region III is absent in curve 1 for the H crystal containing[7] ~1 ppm of background divalent cations. The slope in this region for curves 3–5 is $\frac{1}{2}W_a+E=0.96$ eV, where W_a is the energy of association of the cation vacancy with the impurity (Mg in the present case) ion. Remembering that $E=0.75$, we obtain a value of 0.42 eV for the pair of cation vacancy and divalent magnesuim. The value of W_a thus obtained is in agreement with the value obtained by Stoebe[9] for the magnesium impurity in LiF crystals.

B. Optical Absorption Results

Curve 1 in Fig. 2 shows the optical absorption results obtained with KCl:Mg crystal, containing 2.0 wt% $MgCl_2$ in the melt, prior to additive coloration. It is seen from the figure that there is a sharp optical absorption band at 272 nm with half-width 0.2 eV. The band at 272 nm is similar to that obtained in alkali-halide crystals doped with [2,4,6] Zn, Cd, Hg, or Pb. It is interesting to note that the optical absorption bands in the ultraviolet region have been observed in alkali-halide crystals doped with[2–4,6,10–12] Zn, Cd, Hg, Pb, Ti, Mn, Co, and Ni but not in crystals doped with[5–7] Ca, Sr, and Ba impurities.

A 1-cm³ KCl crystal doped with magnesium and heated in potassium vapors at 560°C colored uniformly in 6 h. The rate of coloration of a magnesium-doped crystal is somewhat similar to that of a pure or Group-II*A* impurity-doped crystals and different from cadmium-doped crystals. A cadmium-doped crystal cannot be colored uniformly,[3,4,7] even in 90 h at 560°C. The concentration of F centers in the cadmium-doped crystals is maximum on the surface and minimum in the central part of the crystal. The concentration of the 310-nm band centers in these crystals is always maximum at the center and minimum on the surface of the crystal.

Curve 2 in Fig. 2 shows the optical absorption results obtained with additively colored (in the dark) KCl crystals doped with 2.0 wt% $MgCl_2$ in the melt. The width of the F band (curve 2) is ~0.38 eV and is not much influenced by Mg impurity. However, the half-width of the 272-nm band seems to have increased slightly and the background absorption seems to have increased in this region. Curve 3 in Fig. 2 was obtained after quenching the colored crystal, in the dark, from 300°C. The optical absorption in the ultraviolet region of the spectrum has increased. Now there is a broad absorption band peaking at ~320 nm and another band peaking at 215 nm. The 215-nm band is presumably due to U centers.[6,7] The potassium-colloidal band peaking at 730–760 nm and observed in pure crystals[6,7] is not formed in these crystals. Curves 4 and 5 show the optical absorption results obtained after quenching the crystal from 400 and 530°C, respectively. It is seen from the figure that with the increase in the temperature of quenching the absorption in the F band, as well as in the 320-nm band regions, decreases. On quenching the crystal from 600°C, all absorption bands disappeared (results not shown in the figure). Similar absorption measurements were also made with additively colored crystals exposed to visible light at room temperature. The absorption at the M, R, and N bands increased at the expense of F centers but no additional bands were produced. The absorption at the 272-nm band did not change on optically bleaching the crystals at room temperature. The results obtained on heating the optically bleached crystals were similar to those shown by curves 3–5 in Fig. 2.

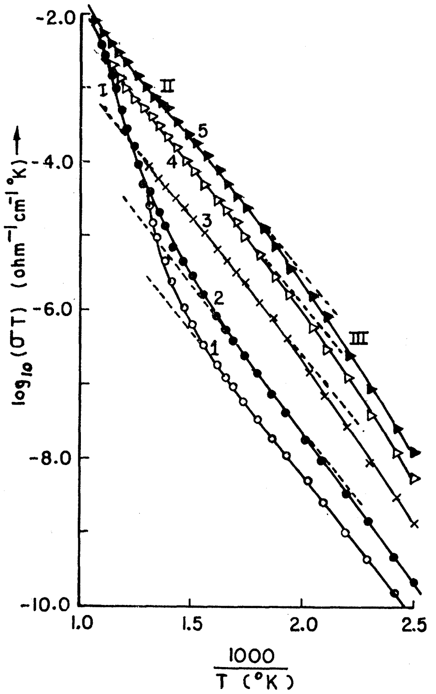

FIG. 1. $\log_{10}\sigma T$ as a function of $1/T$ for highly pure H, pure B, and magnesium-doped D crystals of KCl. Curves 1 and 2 are for the H and B crystals and curves 3–5 for the three D crystals doped with 0.25, 1.0, and 2.0% $MgCl_2$ in the melt.

It is interesting to compare the results with those obtained with crystals doped with Ca, Sr, Ba, and Cd.

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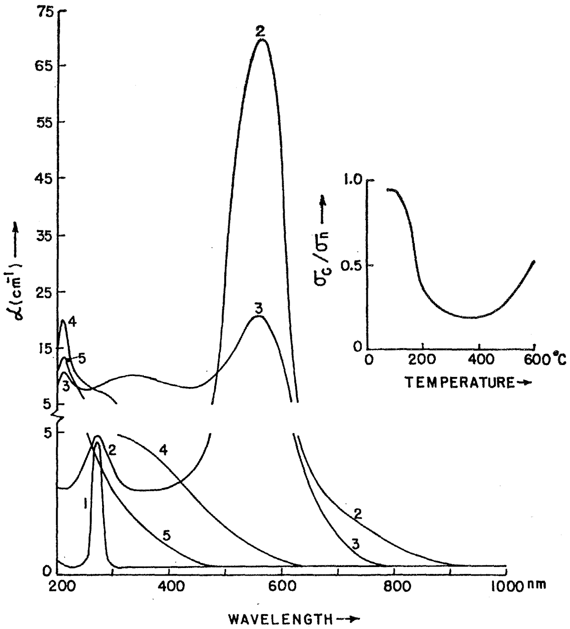

FIG. 2. Optical absorption spectra of uncolored (curve 1) and additively colored (curves 2–5) KCl crystals doped with 2.0 wt% $MgCl_2$ in the melt. Curve 2 is for the quenched, from the coloring temperature, crystal. Curves 3–5 were obtained after quenching the colored crystal from 300, 400, and 530°C, respectively. The σ_c/σ_n-versus-temperature plot for the colored crystal is shown in the inset of the figure.

Alkali-halide crystals doped with Group-II*A* impurities have been studied more extensively.[5,6] It has been found that under suitable conditions of optical and/or thermal bleaching of the colored crystals doped with Group-II*A* impurities, the *Z* bands are formed on the longer (Z_1 and Z_2 bands) and shorter (Z_3 and Z_4 bands) wavelength side of the *F* band. Small concentrations of these impurities promote, whereas larger concentrations suppress completely, the formation of colloids of alkali metal.[7] In Cd-doped crystals, no *F* aggregate bands (on the long-wavelength side of the *F* band) can be formed.[4,7] A band at ~310 nm due to atomically dispersed Cd and another band at ~275 nm due to colloidal cadmium are obtained,[4,7] respectively, in additively colored quenched and colored and bleached crystals at $\geq 500°C$.

C. Conductivity Results

The plot of σ_c/σ_n, where σ_c is the conductivity of the colored crystal and σ_n that of an identical uncolored crystal, as a function of increasing temperature, in the dark, for the KCl crystal doped with 2.0 wt% $MgCl_2$ in the melt, is shown in the inset of Fig. 2. The conductivity ratio σ_c/σ_n remains ~1 up to ~100°C, and starts decreasing thereafter. It becomes ~0.2 near 350°C and then starts increasing. The ratio σ_c/σ_n remains less than unity even up to 600°C. From the figure it can be seen that the excess conductivity due to potassium colloids observed in pure crystals,[7] in the temperature range 300–500°C, is not observed in the magnesium-doped crystals.

The conductivity results obtained with the optically bleached crystals were, in general, similar to those obtained with crystals not exposed to light. The conductivity ratio σ_c/σ_n remained less than unity in the temperature range of 100 to 600°C. In crystals bleached thermally at 500°C and quenched, the ratio σ_c/σ_n became much less than unity even below 100°C (results not shown in the figure).

D. ESR Absorption Results

The uncolored KCl crystals doped with magnesium did not give any ESR absorption. After additive coloration, a single, Gaussian ESR line, with a half-width 46 G and *g* factor 1.9957, characteristic of *F* centers[7,13] in KCl, was obtained. On quenching, the crystal from 50–400°C, in the dark, the *F*-center ESR absorption decreased in intensity, but no additional absorption line was observed. At 400°C, the *F*-center ESR absorption line disappeared completely. The conductivity and the ESR results are consistent with the optical results discussed earlier in this section, and confirm that potassium colloids are not formed in Mg-doped KCl crystals.

Similar ESR measurements were also made with additively colored crystal exposed to visible light. The half-width of the *F*-center ESR absorption line decreased from 46 to 36 G in 45-min exposure to visible light. The *g* factor did not change and no additional line was obtained in the exposed crystals.

The experiments performed with crystals containing different concentrations of $MgCl_2$ show that if the concentration of $MgCl_2$ (in the melt) is $\geq 1.0\%$, the equilibrium density of *F* centers is somewhat reduced (by ~5 to 10%). The other results discussed above are independent of the concentration of $MgCl_2$ (in the melt) in the range 0.25–2 wt%.

4. DISCUSSION

The various models of the impurity centers, which can give rise to absorption bands in the ultraviolet region of the spectrum, are[3] (a) the absorption because of the excitation of the impurity ion inside the crystal, (b) charge transfer from the neighboring halide to the impurity ion, (c) charge transfer from an anion, with the impurity in its first neighbor position, to the alkali metal, and (d) crystal-field spectra of the impurities or the intra-ionic transition. A comparison of the optical absorption results obtained with the uncolored KCl crystals doped with magnesium, with those of earlier authors[3] shows that the 272-nm band may be due to the crystal-field spectra of magnesium impurity or intra-ionic transition as suggested by Kuwabara and Aoyagi.[14]

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The absence of ESR absorption in these crystals prior to coloration suggests that the atomically dispersed magnesium goes into the lattice in the Mg^{2+} state. This is consistent with the conductivity results discussed in Sec. 3A.

Extensive conductivity measurements made with pure crystals[4,7,15] have shown that in additively colored KCl crystals the F centers do not contribute to the conductivity below 400°C in dark. Since in additively colored KCl crystals doped with magnesium the ratio σ_c/σ_n remains ~ 1 up to 100°C, the results indicate that the concentration of positive-ion vacancies does not change after additive coloration, and that during the process of additive coloration the electronic state of magnesium ions does not change. These results are consistent with the observation that the absorption at the 272-nm band peak remains unchanged after additive coloration. The results are different from the results obtained with additively colored KCl crystals doped with cadmium.[4,7] In cadmium-doped crystals the conductivity ratio σ_c/σ_n remains much less then unity, even below 100°C, and an optical absorption band peaking at 310 nm in KCl due to cadmium is observed. The observations that the equilibrium concentration and the rate of growth of F centers in the magnesium-doped crystals at the coloration temperature (560°C in the present case), remains equal to that in the pure or Group-II*A* impurity-doped crystals, and unlike cadmium-doped crystals no new centers are formed during the additive-coloration process, show that the effect of all the Group-II*B* impurities on the coloration properties of alkali halides is not identical. A comparison of the present results with the results of Ben Dor *et al.*[2] shows that the probability of formation of a new center during the process of additive coloration increases as we increase the atomic number of the added Group-II*B* impurity. This is consistent with the ionization potentials of these elements; the ionization potential of magnesium is minimum and that of mercury is maximum.[16] Since the ionization potential of beryllium is slightly greater than that of magnesium, it would be interesting to see the effect of beryllium on the colorability of alkali halides.

The results obtained with crystals quenched from 100–500°C are interesting. Since the conductivity ratio σ_c/σ_n decreases in this temperature range, the results indicate that the concentration of positive-ion vacancies decreases on heating the crystals above 100°C, in the dark or in the light. These results are similar to those obtained with the additively colored KCl crystals doped with Ca or Ba or containing unknown background divalent-cation impurities.[7] Jain and Sootha[7] have shown that, even in the dark, the ratio σ_c/σ_n becomes much less than unity, if the crystal contains large amount of barium. The decrease in the conductivity of the colored crystal doped with barium or containing background divalent cations has been attributed to the elimination of free positive-ion vacancies and formation of Scott R' type of centers.[7] In the magnesium-doped crystals quenched from <400°C, in the dark or in the light, no optical absorption bands on the longer-wavelength side of the F band have been observed. Instead, a broad band peaking at 320 nm is formed (Fig. 2) in these crystals. The centers responsible for this band are unstable above 350°C and disappear completely on heating the crystal at 500°C or above. These results, therefore, suggest that the broad optical absorption band peaking at 320 nm is similar to the Scott R' band, and the centers responsible for this band are aggregates of Mg^{2+}, positive-ion vacancies, and F centers. The observations that the 320-nm band disappears, the conductivity ratio σ_c/σ_n becomes much less than unity even below 100°C, and the 272-nm band does not appear after quenching the colored crystal from 500°C or above, indicate that magnesium impurity diffuses out of the crystal lattice on heating the crystal at or above 500°C.

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