

Colour centres in powdered KI

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Abstract. Fine powder of KI was coloured in an electrodeless discharge. Due to quick bleaching of the F centres produced in this method, it was possible to prepare the samples that were almost free from the F centres. High concentration of the electron deficient centres could be produced, which were studied by measuring the diffused reflectance. A band at 354 nm is shown to be composed of two overlapping bands. Further, growth of a band appearing at 265 nm is studied. Bleaching characteristics of the samples are studied and it is shown that, similar to F centre bleaching, bleaching of these samples also proceeds in at least two steps. The difference between two components of the bleaching curves is quite marked. Further it is showed that the components are related to the presence of different absorption bands and appear at different stages of colouration.

Keywords. Colour centres; reflectance spectra; bleaching characteristics; electrodeless discharge.

1. Introduction

Colour centres in alkali halides are studied very extensively. However, most of the work is confined to single crystals. Very few measurements are available on fine powders or polycrystallites. It is known that colour centres in pellets have properties both similar and dissimilar to those in single crystals (Hersh 1957 *a*, Hersh 1957 *b*). Particularly, V bands in polycrystallites are very stable and the ratio F/V varies largely with irradiation time. Characteristic bands of free halogen are known to appear. However, tri-iodide bands are not well studied. It was noted that these bands are optically stable but extensive bleaching characteristics were not studied. Bleaching characteristics are important to establish a generic relation between different absorption bands.

In the present work a fine powder of KI was coloured in an electrodeless discharge. Due to quick bleedings of the F centres produced in this method, it was possible to prepare the samples that were almost free from F centres. High concentrations of the electron deficient centres could be produced. It is shown that the tri-iodide band can be decomposed in two separate well resolved bands. Further, the growth of a band appearing at 265 nm is studied. Bleaching characteristics of the samples are studied and it is shown that, similar to F centre bleaching of these samples also proceeds in at least two steps. The difference between two components of the bleaching curve is quite marked. Further, it is

shown that the components are related to the presence of different absorption bands and appear at different stages of colouration.

2. Experiment

The experimental set up for electrodeless discharge colouration is described elsewhere (Arnikar *et al* 1971, Mnade and Kanitkar 1970). G. R. grade KI in fine powder form was used without further purification. A Carl Zeiss spark generator HFO₂ was used as a power supply of 12 kV (eff.) 0.45 Mhz to produce the discharge. Different samples were coloured to different extents by adjusting the time of irradiation and the discharge current, the latter depending upon the voltage and pressure of the residual air. Reflectance spectra of the samples so coloured were taken on Carl Zeiss reflectance spectrophotometer VSU 2P with a 45/0 geometry. Bleaching was performed with unfiltered radiation from a tungsten filament lamp.

3. Results

The reflectance curves of the various samples are shown in figures 1-4. For the sake of comparing the spectra with conventional absorption spectra, $\log 100/R$, instead of R , the reflectance, was plotted against the wavelength. Figure 1 shows the typical reflectance curve over the entire spectral range. When reflectance of the coloured samples is measured against freshly prepared NaF surface, only one peak appears at 354 nm. There is catastrophic absorption in the ultra-violet, the tail of which extends throughout the visible range. No peak corresponding to F or any other excess electron colour centres appears. Due to the light produced in the process of discharge these centres are totally bleached. The reflectance

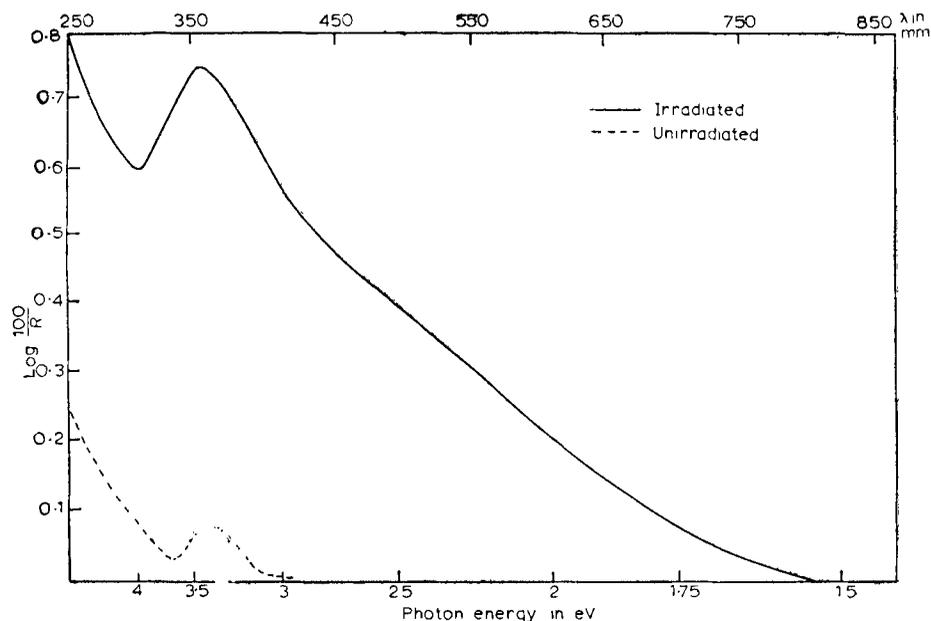


Figure 1. Reflectance spectra of KI, as measured against NaF.

curve of uncoloured KI itself as measured against NaF contains a small amount of the same band. The same observation was made by Hersh also. This is the tri-iodide band. Due to the small amount of the trace moisture which liberates free iodine, it is present in the unirradiated samples also. Colouration enhances this band greatly. To study the irradiation induced absorption, if unirradiated KI is used as standard, one notes that at least two absorption bands peaking at 342 and 384 nm appear in the curves of coloured samples. Such a procedure is not uncommon in the study of single crystals and derives more significance. The visible part of reflectance remains similar in nature and is not of much importance. So all other curves are plotted by employing KI as standard and the visible part of the spectra is omitted, so that more attention can be paid to the highly significant ultra-violet part.

Figure 2 shows irradiation induced absorption bands in samples coloured for different periods. For low colouration two bands peaking at 332 and 384 nm appear. The band at 332 nm is nearly gaussian in shape. The band at 384 nm has a long tail that extends throughout the visible range. With increasing irradiation a tail appears on the short wavelength side of the 332 nm band. With further increase in the colouration a band at 265 nm appears. This band grows fast and soon becomes equal in magnitude to other bands. Meanwhile, the band at 332 nm gradually shifts to long wavelength side and finally to 342 nm whereas the band at 384 shifts to short wavelength side and to a final position of 376 nm. In primary stages of the colouration the band at 332 nm is slightly stronger to the band at 384 nm. In later stages the situation is reversed. Light produced in the process of discharge complicates the matter further as it bleaches the bands at 332 and 384 nm

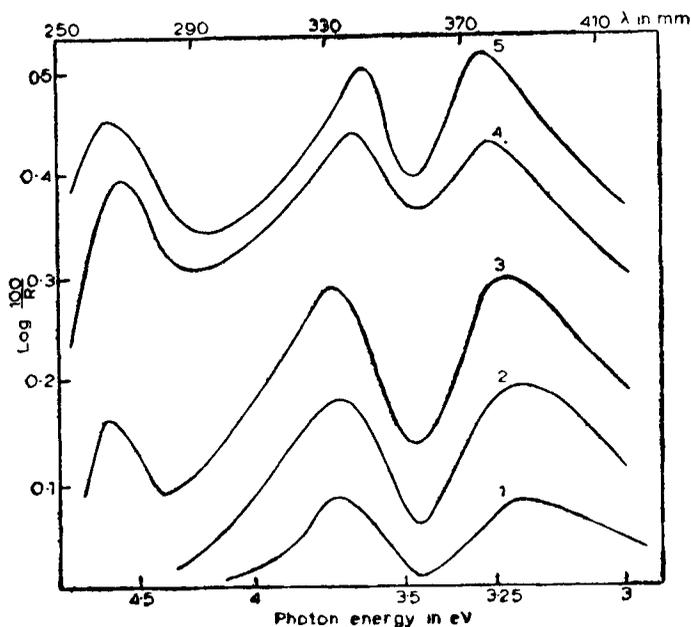


Figure 2. Reflectance spectra of KI coloured for different times. Colouration times (1) five minutes, (2) seven minutes, (3) fifteen minutes, (4) thirty minutes, (5) forty-five minutes.

but not the band at 265 nm effectively. So one often obtains the samples that contain a large band at 265 nm and comparatively smaller bands at 332 and 376 nm. Careful measurements however, show that the 265 nm band appears at latter stages of colouration. This is beautifully demonstrated by the bleaching curves. Meanwhile, visible absorption also increases, without changing its nature, the appearance of the sample changing from brown to brick-red at the same time.

Figure 3 shows bleaching characteristics which are equally instructive. Bleaching was performed by unfiltered radiation from 60 Watt tungsten filament lamp held, at the distance of 10 cm. Y axis refers to the absorption at peak of the band centred round 376 nm. In the absence of 265 nm band, the colouration is quite stable, almost unbleachable. Bleaching curve resembles a straight line rather than an usual exponential one. As the extent of colouration and the band at 265 nm increases, a faster component is introduced in the bleaching curve. However during the bleaching, the band at 265 nm is bleached to lesser extent, though its presence induces a faster bleaching component in other bands. Thus in the topmost curve of figure 3, about 20% of the colouration is removed in the first minute of the bleaching and after that the bleaching curve is almost a straight line. In this part of the curve also, the slope of the line increases with degree of the colouration. For this sample, the reflectance spectra at different stages of bleaching is shown in figure 4. (Similar curves can be obtained for other samples also though on different scales). It is evident that the bands at 342 and 376 nm bleach very rapidly at first and slowly afterwards but not the band at 265 nm. After prolonged bleaching it is even possible to get rid of almost all of the 342 nm and 376 nm bands and still retain 265 nm band. At first sight it may appear that this is perhaps due to the fact that bleaching light contains very less amount of radiation in this range. However, similar results are obtained when ultra violet light is used for bleaching. This clearly shows that fast bleaching is associated with the presence of the 265 nm band.

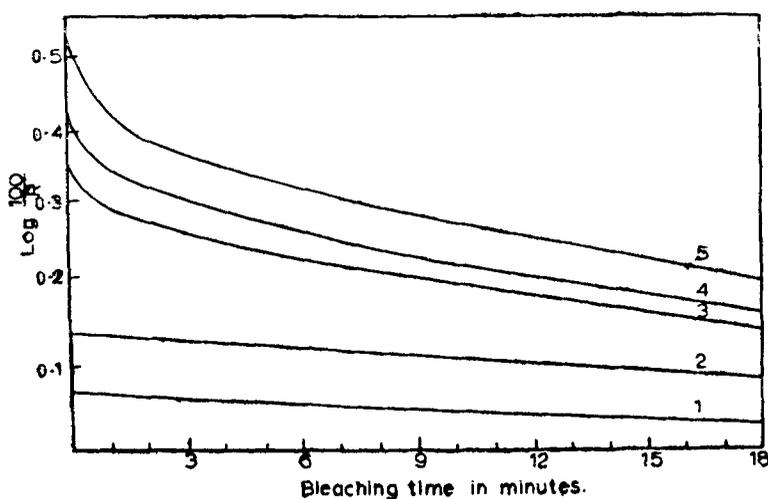


Figure 3. Bleaching Characteristics. (Numbers on the curves specify the same colouration time as in figure 2. Y axis refers to the absorption at the peak of the band at 376 nm.)

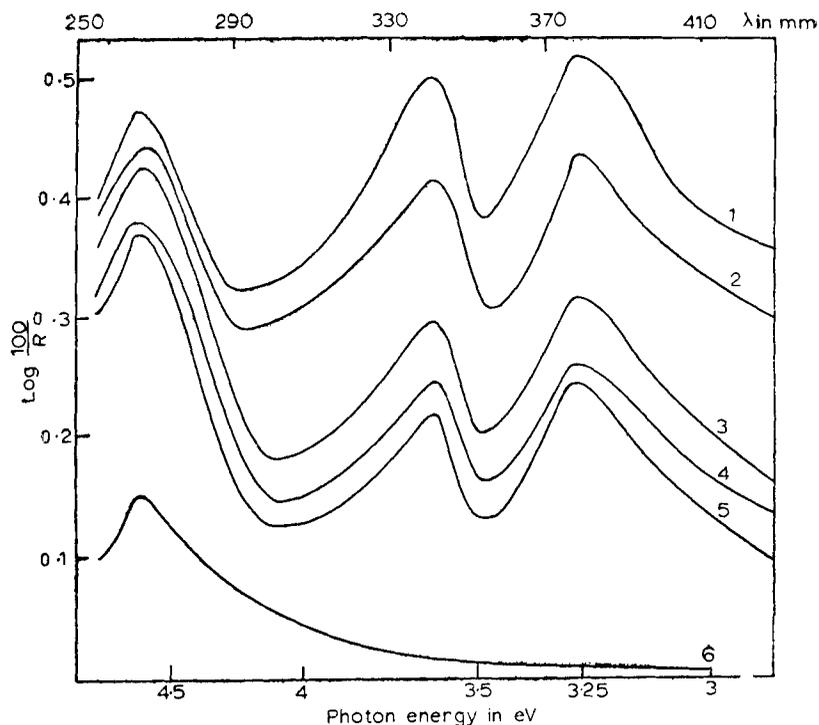


Figure 4. Reflectance spectra of KI at different stages of bleaching. Bleaching times (1) Immediately after the colouration (2) after 1 minute's bleaching, (3) five minutes bleaching, (4) ten minutes bleaching, (5) fifteen minutes bleaching, (6) after prolonged bleaching.

4. Discussion

In an electrodeless discharge, colouration depends on many factors such as current, pressure, intensity and spectral distribution of light produced in the discharge, size of the discharge tube, colouration time and all these factors are interrelated. As far as possible, other parameters were kept fixed and samples were coloured to different extents by varying the colouration time. However, slight change in above mentioned parameters affects the colouration quantitatively, and so some degree of arbitrariness is introduced in the colouration times mentioned in figure 2. For this reason growth of colouration is not discussed.

When measured against NaF, only one well resolved band appears in the reflectance curve at 354 nm which has already been interpreted as V band by previous workers (Mallow 1935 and 1937, Hersh 1957). However Hersh also had observed the V centres in small concentration in unirradiated samples. So to measure the discharge induced absorption unirradiated KI itself should be employed as a reference standard. As we have shown here, this splits the band at 354 nm into two bands and we think that his procedure may have more significance. It may help to remove the discrepancy that exists in the peak positions of V bands produced by additive colouration and x-ray irradiation.

The band that we have observed at 265 nm is very similar to that observed by Uchida and Nakai (Uchida 1954) and Bronstein and Noble (1956) at the same wavelength. These workers also observed that this band is thermally, as well as

optically, stable. It remains even if the other bands are completely bleached by optical or thermal treatment. Again the half-width calculated by Uchida and Nakai, 0.5 eV, is very close to the value 0.58 eV that we have observed. The small difference can be attributed to the scattering effect inherent in the diffused reflectance. Thus we conclude that the band we have observed is the same band as observed by these workers. However, they obtained this band as a short wavelength shoulder of V bands. Hersh argued that this band is not connected to V bands and its identity as an electron deficient centre characteristic of the pure state is questionable as it can be retained in absence of the V bands. Evidence presented here, however, shows that this band is closely related to the bands at 332 nm and 384 nm as its growth induces a fast component in bleaching of these bands. Another significant thing is that, in single crystals this band appears as a small hump whereas in powdered form it shows very prominently. It is quite possible that this is related in some way to the deformations that are inherent in the powders. Thus, deformations are known to influence the excess electron centres quite markedly (Clark and Crawford 1973). A band, known as E band, which grows rapidly, appears in the vicinity of the usual F band. With increasing amount of deformation this band grows and masks the F absorption. Absorption extends over a wide spectral range and resembles KI:TI in many respects (Hersh 1969 and 1967). This band had been attributed to the electrons trapped at the debris. The nature of the absorption, peaking at 265 nm, is very similar to this, especially in that its tail extends throughout the visible range and resembles bleached KI:TI in that there is no resolved F centre absorption. Thus, from these similarities and spectral position, this may be attributed to the holes trapped at the debris. This explains its formation at latter stages. Thus, as a primary product of irradiation, V centres are produced. Due to light produced in the discharge, holes are released from the traps and recaptured at the debris. As this band grows, this retrapping action is enhanced. This may introduce a fast component in the bleaching curves. However, this can take place when colouration and bleaching takes place simultaneously. Colouration may be necessary to provide the sufficient number of V centres. As seen from bleaching curves external bleaching in absence of simultaneous V band production does not result in the 265 nm absorption. Interpretation of this band as a hole trapped at deformations also explains why it appears prominently in the powders and not in single crystals, as in powders high dislocation densities are to be expected.

At present this seems to be a speculation but this can be further tested by observing the intensity variation of this band with the amount of deformation in single crystals. Search for this band in other alkali halides also may prove useful. To our knowledge, influence of the deformations on the properties of electron deficient centres, however, has not been studied in details.

Acknowledgement

We wish to express our sincere thanks to H N Hersh of Zenith Radio Corporation, Chicago, USA for his stimulating communications.

Note: Hersh (private communication) suggests that the two components bleaching is due to two physical intertwined subsystems existing in our samples, one the "perfect" lattice subsystem and the other the imperfections (made up of dislocations, etc.) which bound the indestructible small regions within each crystallite.

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