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Reflectance spectra and thermoluminescence of alkali halides coloured in an electrodeless discharge

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Abstract. Microcrystalline powders of NaCl, KCl and KBr are coloured in electrodeless discharge. Reflectance and TL studies of these coloured powders are reported. It is concluded that colouration of powders can be understood by considering them as an admixture of perfect and imperfect lattices, and differs from that of single crystals. It is suggested that some of the descrepancies reported on TL data may be due to such a difference. Further, it is shown that a better correlation can be had if TL data are presented along with the corresponding optical measurements. Adoption of such a procedure may help to remove the descrepancy in TL data.

Keywords. Colour centres; thermoluminescence; plastic deformation; reflectance spectra; electrodeless discharge.

1. Introduction

Colour centres and thermoluminescence in alkali halides have been studied for a number of years (Compton and Schulman 1962, Fowler 1968). However, most of the colour centre measurements are confined to single crystals though the powders are often used in the thermoluminescence experiments. Powders provide an interesting system in that there exist two physically intertwined subsystems. One the ' perfect ' lattice subsystem and the other the imperfections (made up of dislocations, etc.) which bound the indestructible small regions within each crystallite (Hersh: private communication). These two subsystems possess different colouration characteristics. Thus, aggregation processes are different in the imperfect lattice. The absorption bands corresponding to different F aggregate centres are no more Gaussian in shape due to the overlapping of E band related to the presence of dislocations (Ueta and Kanzig 1955, Crawford and Clark 1973). Effect of deformation on the thermoluminescence is also well known. (Jain and Mehendru 1965, Mehendru and Radhakrishnan 1969, Crawford and Clark 1973). It is known that deformation produces a glow peak at 250°C in the glow curve of KCl besides the usual glow peaks at 135°C and 185°C characteristic of the perfect lattice (Jain and Mehendru 1965). Thus, in the powders it would be interesting to observe which way the colouration characteristics of two subsystems interact.

In the present paper, we report the thermoluminescence and colour centre studies of the microcrystalline powders of NaCl, KCl and KBr. Powders bleach rapidly with a low yield of F aggregate centres. The interaction of dislocations, on the other hand, is reflected through the F aggregate centres. To overcome this difficulty, the electrodeless discharge method of colouration was chosen, as *F* aggregate centres in large concentrations are reported for the salts coloured by this method (Moharil and Deshmukh 1976).

2. Experimental

The experimental set up for producing an electrodeless discharge is described in literature (Arnikar *et al* 1971, Moharil and Deshmukh 1976). G R grade salts from Sarabhai-Merck were used without further purification. Carl Zeiss spark generator HFO_2 was used as a power supply of 12 kV (eff), 0·45 MHz to produce the discharge. To study the colour centres so formed, diffused reflectance from the coloured powders was studied on the Carl Zeiss reflectance spectrophotometer VSU 2P, with a 45/o reflectance attachment. All the measurements were carried out at 300K. The bleaching was performed by a 100 W tungsten filament lamp held at the distance of 15 cm from the samples in conjunction with an appropriate corning glass filter.

Thermoluminescence from the samples was detected by RCA 931A photomultiplier and recorded on the DIGILOG potentiometric strip chart recorder. Heating rate of 50/min was used. Most of the glow peaks were observed below 210°C, above which the rate of heating drops considerably. A heating rate curve is also given along with each glow curve.

3. Results

Figure 1 shows the reflectance spectra of the different coloured samples. Uncoloured samples themselves were employed as reference standards. To compare the spectra with the conventional absorption spectra, log (100/R,) instead of *R*, the reflectance is plotted as a function of wavelength. The peaks at 465 nm, 560 nm and 630 nm in

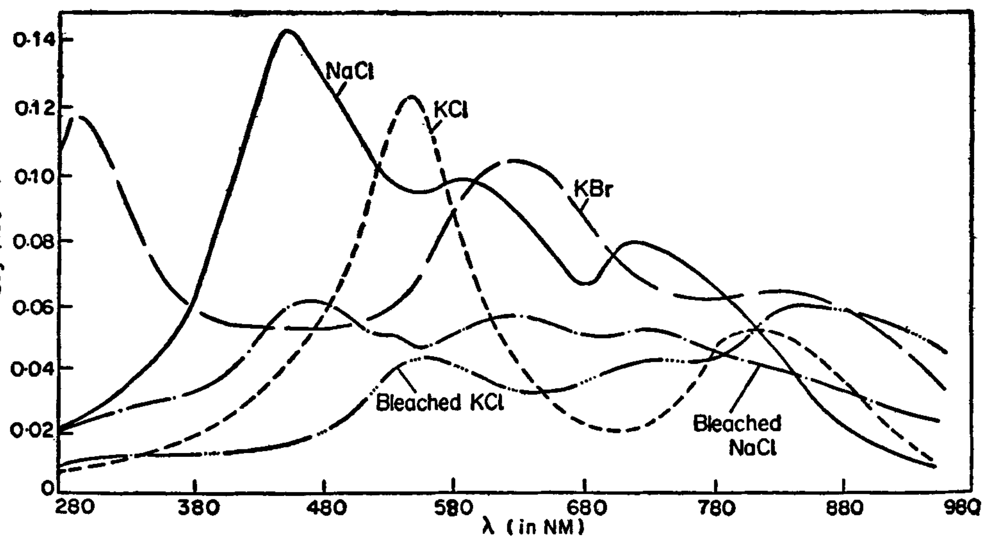

Figure 1. Reflectance of coloured samples.

the reflectance curves of NaCl, KCl and KBr respectively correspond to *F* centre absorption. There is a broad absorption on the long wavelength-side of *F* centre absorption maxima. A kink appears at the position of *M* band absorption maxima in the reflectance curve of KBr. In the case of NaCl and KCl, the *M* bands at 720 nm and 820 nm respectively are comparatively well resolved. A small kink appears at 590 nm for NaCl and 730 nm for KCl, corresponding to *R* centre absorption. *F* centre absorption tails throughout the near ultra-violet. In the case of KBr, on the other hand, absorption increases again in this region. This absorption represents a long wavelength tail of the tribromide absorption at 285 nm (Hersh 1957a).

When the discharge conditions are adjusted to produce an intense glow, reflectance spectra are very much affected. The curves (2 and 4 of figure 2) are in general very broad. Maxima corresponding to different colour centres can just be distinguished, if these samples are further bleached by external light after the colouration is stopped. During the initial stages of bleaching, a decrease in the *F* band absorption is accompanied by an increase in the absorption at longer wavelengths. In the later stages, overall absorption decreases, but not in a uniform manner. During this stage of bleaching, absorption prevails in the *M* band region in KCl and *R* band region in NaCl. Absorption of KCl resembles that reported by Ueta and Kanzig (1955) for deformed single crystals. Reflectance spectra during this final stage are included in figure 1. It was observed that for NaCl the apparent increase in *F* band half-width during the bleaching is asymmetric. This is shown by giving the bleaching curves in figure 3. Half-width of the high energy side of the *F* band (W_R) profile increases fast, whereas the increase in the half-width of the low energy side (W_L) is not so marked. These half-widths are plotted as a function of ratio M/F in the insert of

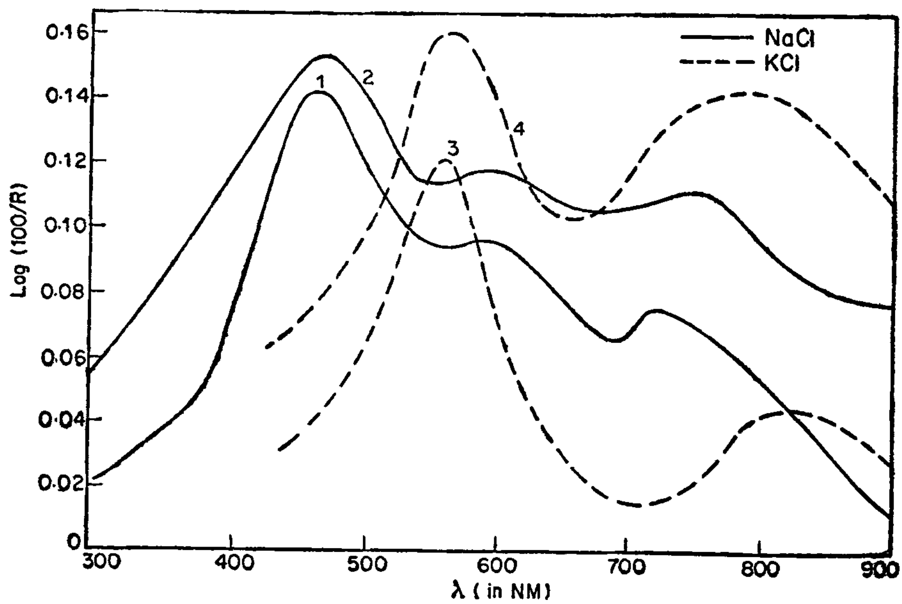

Figure 2. Reflectance spectra of NaCl and KCl coloured under different conditions. 1. NaCl. 2. NaCl coloured under intense glow conditions. Optical absorption on the long wave lengths side of *F* centre absorption maxima is enhanced and broadened. 3. KCl. 4. KCl coloured under intense glow conditions. Again the long wavelength wide absorption is enhanced with broadening, presumably due to *E* centre formation.

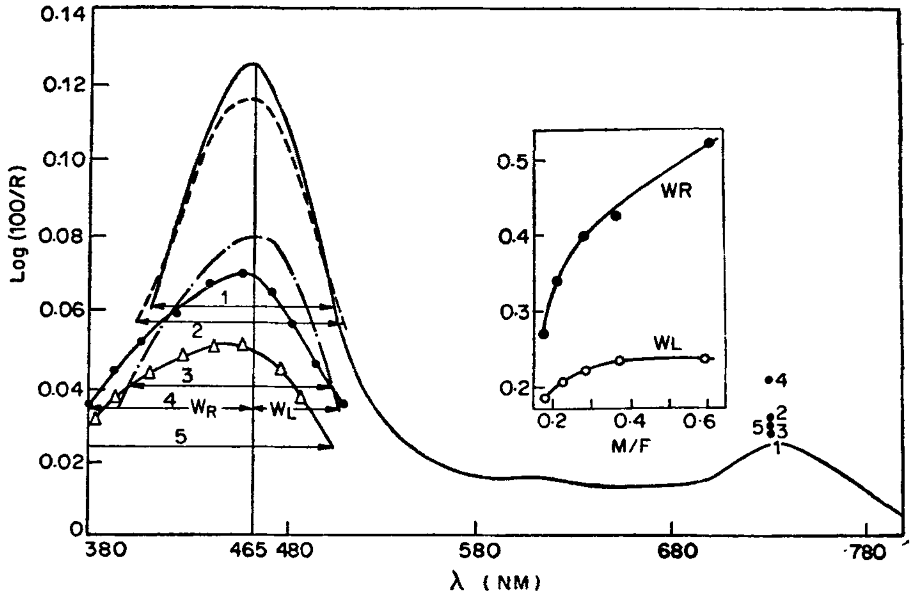

Figure 3. Bleaching of coloured NaCl by F band light. Bleaching time 1. as irradiated 2. 2 min. 3. 5 min. 4. 10 min. 5. 20 min. Arrows mark the half-width of the higher and lower energy side of F centre absorption maxima (W_L and W_R), which are plotted as a function of the ratio M/F in the insert. Points marked 1-5 indicate absorption at the peak of M band.

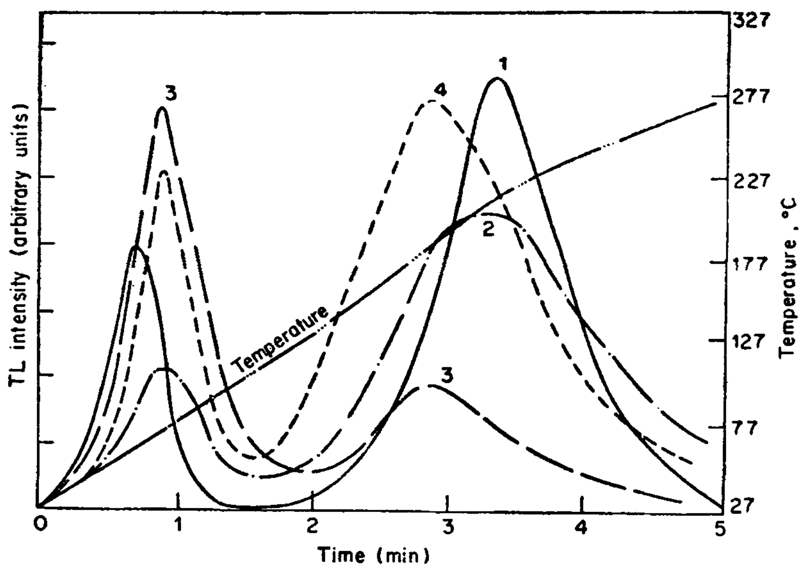

Figure 4. TL glow curves of the samples of figure 2. Numbers on the glow curves specify the same colouration as in figure 2. Temperature curve is also given.

figure 3. This asymmetric broadening imply the formation of some absorption band, appearing as a bleaching product, hidden under the F band absorption. In the case of deformed single crystal of NaCl, a kink has been observed on the high energy side of F band (Arcenovici and Townsend 1972, Corradi *et al* 1975). Earlier

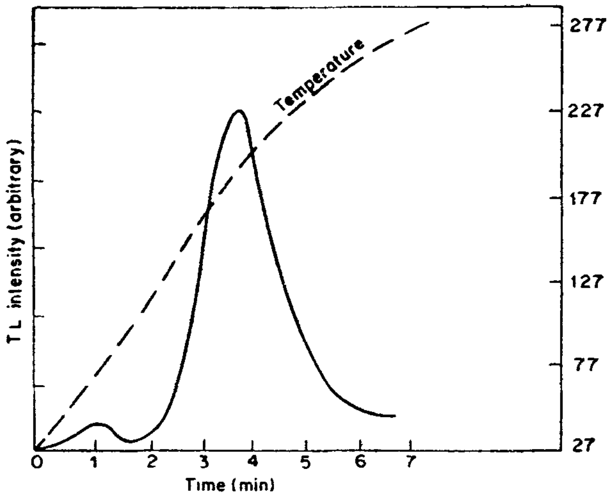

Figure 5. TL glow curves of KBr coloured in an electrodeless discharge.

workers have attributed this kink to the different kind of F centres. However, it will not be proper to conclude that this kink represents E band absorption maxima, as in potassium halides, the E band absorption maxima is known to appear at the wavelengths longer than F band maxima (Hersh and Cocoo 1967). Presently, the asymmetric broadening is to be identified with the deformational effect. Bleaching, thus, clearly indicates a marked influence of dislocations, and so a similar influence was expected to be reflected in the thermoluminescence curves, which are described next.

Figure 4 shows the TL of different coloured samples of figure 2, and figure 5 shows a typical glow curve of KBr. In each case two glow peaks, rather well resolved, appear. The glow temperatures are 77°C and 186°C for KCl, 64°C and 218°C for NaCl and 86°C and 186°C for KBr. Considering that the peaks are sufficiently well resolved, detailed analysis of the glow curves regarding the trapping parameters was undertaken. The basic quantities used are, T_m, the glow temperature, T_1 and T_2 the temperatures at which TL emission falls to half of its maximum value, on the high and low temperature side of T_m, respectively. Chen's (1969) equations of general order kinetics were used. Three equations are—

$$E_\tau = [1{\cdot}51 + 3\,(\mu_g - 0{\cdot}42)]\,\frac{kT_m^2}{\tau} - [1{\cdot}58 + 4{\cdot}2\,(\mu_g - 0{\cdot}42)]\,2kT_m$$

$$E_\partial = [0{\cdot}976 + 7{\cdot}3\,(\mu_g - 0{\cdot}42)]\,\frac{kT_m^2}{\partial}$$

$$E_\omega = [2{\cdot}52 + 10{\cdot}2\,(\mu_g - 0{\cdot}42)]\,\frac{kT_m^2}{\omega} - 2kT_m$$

where, $\partial = T_2 - T_m$, $\tau = T_m - T_1$, $\omega = T_2 - T_1$ and $\mu_g = \partial/\omega$

Table 1. Trapping parameters derived from the glow curves using Chen's formulae.

	T_m	τ	∂	ω	μ_g	E_τ	E_∂	E_ω
KCl	337K	18	19	37	0·513	0·925	0·918	0·927
KCl	459K	29	30	59	0·52	1·078	1·010	1·1
NaCl	320K	12	13	25	0·52	1·358	1·283	1·326
NaCl	491K	38	25	63	0·396	0·660	0·664	0·665
KBr	459K	37	45	82	0·548	0·749	0·752	0·746

E values are expressed in eV.

The calculated values are presented in table 1. Curves 2 and 4 correspond to the colouration carried out under the intense glow and the corresponding reflectance curves are 2 and 4 of figure 2. In the case of NaCl this curve differs from the previous (curve 1) in that the peak at 218°C is very broad. From the shape it appears that it is composed of two or more glow peaks, but the usual method of isolating failed to show any. In the case of KCl the glow peak at 186°C is very much enhanced as a result of the intense glow condition of discharge. This peak is also broad, but the method of repeated TL cycles yielded no other glow peak.

4. Discussion

Influence of the plastic deformation on TL of NaCl and KCl is well known. Ausin and Alvarez-Rivas (1972) have reported a broadening of the glow curve as a result of plastic deformation of NaCl. Jain and Mehendru (1965) have made a detailed study of TL of KCl. They have found two glow peaks at 135°C and 185°C. The peak at 135°C saturates soon and the one at 185°C appears during the later stages of colouration. Peaks at lower temperatures have been attributed to the impurities. They have observed another peak at 250°C which has been attributed to the deformations. Ratnam and Garita (1975a) on the other hand, observed the same glow peak in the undeformed specimens also. In this light, appearance of the glow peak at 185°C accompanied by the prominent E centre absorption is not much more conclusive. Thus, our optical results show the marked influence of plastic deformations. In TL, on the other hand, we do not observe a 250°C which should accompany the deformational effects. If the peak that we have observed at 186°C is to be identified with the 185°C peak of Jain and Mahendru (1965), then our TL results show no correlation with absorption measurements. Perhaps, our results can be best understood on the basis of the experiments of Ueta and Sugimoto (1962) and Ueta *et al* (1962), who studied the effect of deformation and ultra-violet irradiation on the glow curve of KCl. They observed four glow peaks at 80°C, 158°C, 200°C and 250°C peaks were almost independent of the origin and thermal history of the samples. They have attributed the first three peaks to the combined action of ultraviolet light and deformations. They also mention that the peak at 250°C is very much susceptible to optical bleaching. We thus conclude that the glow peaks observed in KCl powder represent a combined effect of plastic deformation and ultraviolet irradiation (by the light produced in the discharge itself). This is then consistent with the results on optical absorption.

Results on the TL of undeformed crystal of KBr are rather confusing. Mehendru and Radhakrishnan (1969) report only two glow peaks at 90°C and 150°C, whereas Murthi *et al* (1971) (as quoted by Hageseth 1972) report four glow peaks for KBr and KBr:Cu at 86°C, 104°C, 119°C and 186°C. In specpure KBr, Hageseth (1972) reports only one glow peak at 152°C. He also observed an additional kink at 185°C in the samples which were not properly annealed out and assigned it to some localized defect other than *F* centre. Levingson *et al* (1973) have questioned this assignment. They have observed three glow peaks at 100°C, 150°C and 180°C, and attributed all these to *F* centres. Recently Ratnam and Garita (1975b) have observed three glow peaks at 92°C, 152°C and 180°C. If Hageseth's conclusion is to be followed, then the interpretation of our results is that the TL behaviour of KBr powder is similar to that of an extremely deformed single crystal, consistent with optical measurements. On the other hand, if the results of Murthi *et al* (1971) and Ratnam and Garita (1975b) are to be followed then the conclusion is that the TL of KBr is not influenced by plastic deformations, contrary to the optical absorption measurements but consistent with the observation of Mehendru and Radhakrishnan (1969). It appears that more experiments on the TL of deformed single crystals of KBr will be required to clarify the matter.

We are afraid that not much can be discussed about the trapping parameters presented in table 1. It is difficult to compare our results with literature values. There are so many sets of values available that one wonders whether any value of these parameters can be shown to agree with one of them with so many to choose from. An example of NaCl may be sufficient to illustrate this point. Hill and Schwed (1955) report the same value of trap depth for all the glow peaks. A similar observation was made by Bonfiglioli *et al* (1959), but their value of 0·72 eV is far too small from that of 1·25 eV reported by Hill and Schwed (1975). Aramu *et al* (1966), on the other hand reports 1·1 eV for glow peak at 368K and 2·06 eV for the glow peak at 597K. The analyses, accordingly, lead to different conclusions. In fact, trap depth values determined by the different methods from the same set of observations vary radically. Ausin and Alvarez-Rivas (1972) have calculated the *E* values for 320K glow peak of KCl by ten different methods, which range from 0·16 eV to 0·79 eV. Perhaps some of the descrepancies in values reported by different workers arise from the mistakes in identifying the glow peaks.

It appears from the optical absorption that the powders can be considered as an admixture of two physically intertwined subsystems—one the perfect lattice subsystem and the other the imperfections (made up of dislocations, etc.) which bound the indestructible region within each crystallite. The results on TL, on the other hand, are not unequivocal. This disagreement between the TL and optical data, however, is not disheartening, but rather to be anticipated, since the TL and optical measurements ascribe different properties to trapped electron. Thus, TL is known to show the presence of two or more types of *F* centre for which optical absorption is identical (Jain and Mehendru 1965). Again, *F* centre absorption maxima show a regular sequence governed by Mollow-Ivey type relation, whereas thermal trap depth of a trapped electron in different matrices as determined from TL glow curves, or even the positions of TL glow peaks, do not obey any sequence. As far as the influence of plastic deformation is concerned, a possible reason for such a descrepancy in the TL and optical data is that the agencies through which the interaction of trapped electron and deformations takes place might be different in two cases. Thus, the optical absorption is influenced by the debris left behind by the dislocations during their motion occurring as a result of plastic deformation, whereas the TL may be influenced much more directly by the plastic deformations.

Be that as it may, it can still be concluded that the effect of deformation is bound to show up in the colouration of powders. In optical absorption experiments single crystals are invariably used. In TL experiments, on the other hand, powders are used very often. As the colouration by ionizing radiations is performed in dark, the effect of plastic deformations may not show up. But if the powder is exposed to light, intentionally or otherwise, the effect of deformations is bound to show up as indicated by our results. Some of the inconsistencies in different TL results reported may be due to such reasons. The TL curves might prove more useful when given along with the corresponding optical absorption. This may help in understanding the different results. Particularly, if a correlation can be set up between a TL glow peak and optical absorption band, then the information derived from the optical studies for the corresponding centre can be used in analysis of that glow peak.

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