

Reflectance spectra and thermoluminescence of NaBr coloured in an electrodeless discharge

S V MOHARIL and B T DESHMUKH

Department of Physics, Nagpur University, Nagpur 440 010

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Abstract. A comparative study of the optical and thermoluminescent properties of γ irradiated NaBr and NaBr coloured in an electrodeless discharge is reported. In discharge coloured NaBr F centre absorption maxima shifted with the colouration time. This is tentatively attributed to the formation of E centres. Correspondingly, an additional peak was observed in thermoluminescence glow curve. It is suggested that the results are not characteristic of the method of colouration but rather of the imperfections inherent to the powders, and in a perfect (undeformed) single crystal such a phenomenon should not be observed.

Keywords. Electrodeless discharge; colour centres; thermoluminescence; reflectance spectra.

1. Introduction

Colour centres in alkali halides have been studied extensively for the last several years (Compton and Schulman 1966; Fowler 1968). However, most of the work is confined to single crystals and measurements on the microcrystalline powders are few. It is known that paramagnetism and colour centres can be induced in alkali halides excited by Tesla discharge. Samples treated in ac corona discharge are known to emit light pulses (Westermarck and Graprengeisser 1960). Following these initial experiments, alkali halides were coloured in an electrodeless discharge and their properties were studied (Arnikar *et al* 1971). It was found that powders could be efficiently coloured by this method. Further, the colouration was claimed to possess some properties characteristic of the method of colouration. New bands were found in the aquoluminescence spectra (Arnikar *et al* 1971). A high concentration of F aggregate centres has also been reported in the powders so coloured (Moharil and Deshmukh 1976).

Reports on the study of colour centres in NaBr are very few in the literature. This is partly due to the fact that energy required to produce one F centre is rather high or in other words the efficiency of colouration is low (Rabin and Klick 1960); and partly due to the highly hygroscopic nature of the crystal. Particularly, no mention of the experimental values for the absorption maxima of the F aggregate centres, apart from the empirically predicted (Mollow 1931) values, is made. With the idea that the colouration may be carried out with ease and the observation of the F aggregate centres may be rendered possible by this method of colouration, and also to examine the claims made, a study of the colour centres in NaBr produced by the

electrodeless discharge was undertaken. Interesting results obtained during this investigation are presented in this paper.

2. Experimental

The experimental set up for producing an electrodeless discharge is described in literature (Arnikar *et al* 1971; Mande and Kanitkar 1977) and only essentials will be briefly mentioned here. The discharge tube is an all glass ozonizer. A copper electrode is inserted inside the inner tube and the outer portion is covered with a thin aluminium foil kept pressed against the glass surface serving as another electrode. Powder of the substance to be coloured is filled loosely in the annular space and the discharge tube is then evacuated and high voltage is applied to produce the discharge.

A Carl Zeiss spark generator HFO₂ was used as a power supply of 12kV (eff.), 0.45 MHz. GR grade NaBr from E Merck was used without further purification. Diffused reflectance from the coloured samples was measured as a function of wavelength on Carl Zeiss reflectance spectrophotometer VSU-2P with a 45/0 geometry in the spectral range 270 nm to 800 nm. It was found that when LiF was employed as a reference standard, reflectance curves are very broad due to the self absorption of NaBr prior to the irradiation. Measurements were therefore, repeated by employing uncoloured NaBr itself as a reference standard so that only colouration induced absorption was measured. All the measurements were made at room temperature. Thermoluminescence from the coloured samples was detected by RCA 931A photomultiplier and recorded on DIGILOG potentiometric strip chart recorder. A uniform rate of 40°/min was used for heating.

To compare the colouration produced by electrodeless discharge with that produced by the conventional methods, the powder of NaBr was exposed to γ rays (4.2×10^5 r) from ⁶⁰Co source and similar measurements were carried out on it.

3. Results

Figure 1 shows the reflectance curves of γ irradiated NaBr as measured against LiF as a reference standard. For the sake of comparing the spectra with the conventional spectra, $\log(100/R)$, instead of R , the reflectance was plotted as a function of wavelength. The peak appearing at 540 nm is very broad and corresponds to F centres. Half width is 0.79 eV as compared to the reported value of 0.52 eV (Dawson and Pooley 1969). However, part of the broadening is due to the self absorption of NaBr in an uncoloured state. In the ultra-violet region, a sharp peak, probably due to the tribromide absorption, appears near 300 nm. The tail of this absorption extends up to 400 nm and a small kink near 320 nm can also be distinguished. Again, part of this absorption is due to the absorption of NaBr in an uncoloured state. So, in order to study the colouration induced absorption, reflectance measurements were made by employing the uncoloured NaBr itself as a reference standard (curve 2 of figure 1). In this curve also visible absorption peaks at 540 nm as expected but the absorption in ultraviolet is clearly resolved. There is a sharp peak at 290 nm corresponding to tri-bromide absorption (Hersh 1957). The other peak at 310 nm is not identified but may correspond to an electron deficient centre. A quick search of literature revealed

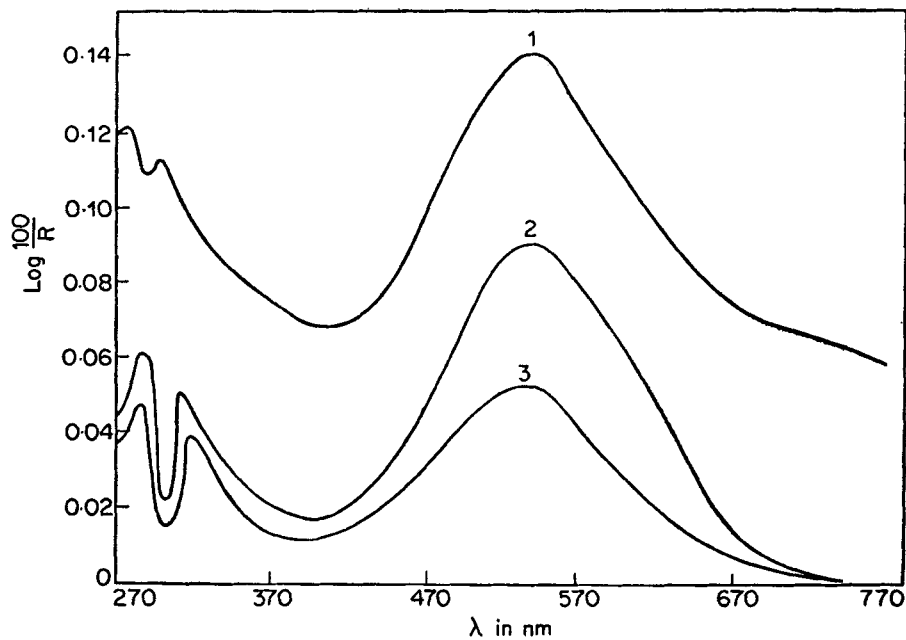


Figure 1. Reflectance spectra of irradiated NaBr: 1. against LiF 2. against un-irradiated NaBr 3. after 5 min. *F* band bleaching against unirradiated NaBr.

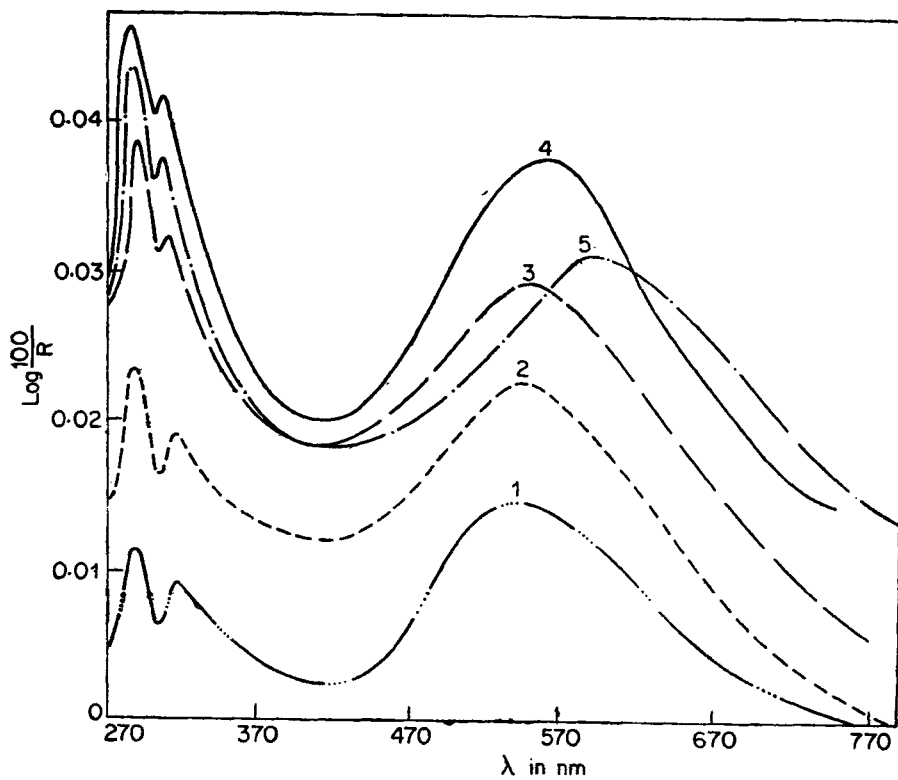


Figure 2. Reflectance spectra of discharge coloured NaBr against unirradiated NaBr; Colouration times: 1. 15 min. 2. 30 min. 3. 1 hr 4. 2 hr 5. 8 hr. Multiply the scale by 2.

no information regarding the V bands in NaBr. Following these results, all other curves are plotted using uncoloured NaBr as a reference standard. Such a procedure is not uncommon in studies of single crystals but is not fully justified in the case of diffused reflectance. Thus our measurements will only be qualitative. However, this simplifies the task of interpretation.

Reflectance curves of NaBr coloured in an electrodeless discharge as measured against the uncoloured NaBr itself, are shown in figure 2. For the low colouration time (15 min.), the reflectance curve is very much similar, but reduced in magnitude, as compared to the reflectance curve (of figure 1) of γ irradiated NaBr. As the colouration time is increased the overall absorption increases, but not uniformly. It is known that in polycrystalline samples, the ratio of V centre of F centre concentration does not remain constant (Hersh 1957). Another interesting fact is that with increasing colouration the time absorption maxima also change, gradually and continuously, to the long wavelength side. Finally for the colouration time of 8 hr absorption maxima occur at 590 nm. It was thought that heavily γ irradiated NaBr may also show such a shift. A sample of NaBr was therefore exposed to a dose of 10^7 r. However, both the optical absorption and thermoluminescence spectra of this sample were not different though enhanced than that of the sample exposed to 4.2×10^5 r and hence are not included in figures 1 and 3. Optical absorption of dis-

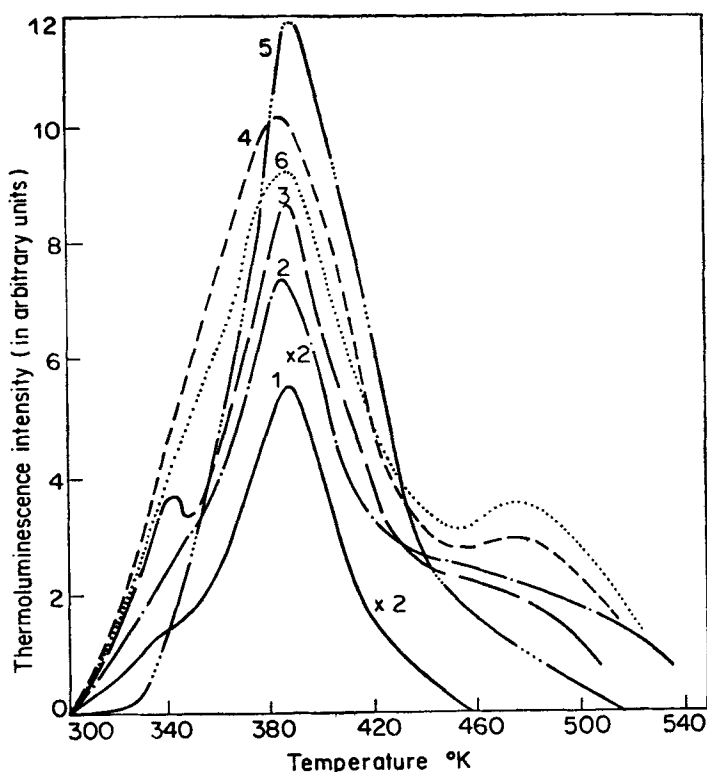


Figure 3. Thermoluminescence of NaBr: 1. Coloured in an electrodeless discharge for 15 min. 2. Same for 1 hr. 3. 2 hr. 4. 8 hr. 5. Irradiated NaBr. 6. NaBr of 4. after isothermal bleaching at room temperature for 24 hr. The first two curves are amplified by a factor of 2 and then reproduced.

Table 1. Trap depth values for different glow peaks

T_m	τ	δ	ω	μ_g	E_τ	E_δ	E_ω
335 K	16	33	49	0.551	2.07	1.87	1.967
390 K	25	30	55	0.454	0.942	1.027	0.994
480 K	29	31	60	0.483	1.50	1.57	1.54

E values are expressed in eV

charge coloured NaBr is thus very much different and a similar difference in the thermoluminescence glow curves was looked for and is described next.

Figure 3 shows thermoluminescence glow curves for different coloured samples. In γ irradiated sample only one prominent glow peak appears at 390 K, but there is a small shoulder at 335 K which is seen rather prominently with increase in the colouration time up to 1 hr. There is also a plateau near 480 K on the high temperature side of the prominent glow peak. With further increase in the colouration time, the kink at 335 K merges in the initial rising part of the main glow peak. Emission on the high temperature side, on the other hand, becomes prominent and a distinct peak appears at 480 K after 8 hr of colouration. Trap depth values for the different glow peaks are listed in table 1. 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 low and high temperature side respectively. Chen's equations (Chen 1972) of general order kinetics were used. Three equations due to Chen are

$$E_\tau = [1.51 + 3(\mu_g - 0.42)] \frac{kT_m^2}{\tau} - [(1.58 + 4.2(\mu_g - 0.42)) 2KT_m]$$

$$E_\delta = [0.976 + 7.3(\mu_g - 0.42)] \frac{kT_m^2}{\delta}$$

$$E_\omega = [2.52 + 10.2(\mu_g - 0.42)] \frac{kT_m^2}{\omega} - 2kT_m$$

where $\delta = T_2 - T_m$, $\tau = T_m - T_1$ and $\omega = T_2 - T_1$, μ_g is the ratio ∂/ω and known as form factor deciding the order of kinetics.

It was thought that the difference in γ ray colouration and discharge colouration is due to the difference in the experimental conditions. Thus, the former is carried out in total darkness whereas in the latter method a rather intense light, which is produced in the discharge as a glow of the residual air, is present. To study the effect of light, γ irradiated sample was bleached by the F band light and corresponding changes in the reflectance spectra and the thermoluminescence glow curve were looked for. Figure 1(3) shows the reflectance curve of γ irradiated NaBr after bleaching. There is a uniform decrease in the absorption; otherwise the nature of the absorption remains the same and is different from the absorption of discharge coloured NaBr as indicated by figure 2. Thermoluminescence also remains the same but is reduced and therefore not reproduced in figure 3. Again, if the difference in the behaviour of γ irradiated

NaBr and discharge coloured NaBr is due to the light, then this should be enhanced after bleaching. So similar bleaching experiments were performed on the discharge coloured NaBr. In the first minute of bleaching there is about 40 per cent decrease in the absorption in ultraviolet. This is followed by a very slow bleaching thereafter. Bleaching of the trihalogen absorption is discussed in detail elsewhere (Moharil and Deshmukh 1976b). Due to such bleaching characteristics, it was difficult to note the corresponding simultaneous changes in the glow curves. Nevertheless, it is seen that the external bleaching cannot bring out the same optical absorption as that brought out by the prolonged colouration. The same should also hold good for the thermoluminescence. Discharge coloured NaBr was allowed to bleach isothermally at room temperature for 24 hr. Glow curve of this sample is shown in figure 3(6). The peak at 480°K grows at the cost of the peak at 390°K. Optical absorption, however, remains more or less the same and so is not shown in figure 2.

4. Discussion

In the study of single crystals it is a common practice to measure the absorption of the coloured crystal relative to that of the uncoloured one. However, in the case of powders, such a procedure may not be fully justified. Thus, the colour centre concentrations deduced from the reflectance may not be correct. However, due to the limitations of diffused reflectance itself, the measurements are relative and depend upon the parameters other than colouration such as particle size and detector geometry, etc. (Buxton and Duley 1974). In our previous studies (Moharil and Deshmukh 1976 a, 1976b) it was shown that despite these difficulties, diffused reflectance can be used to identify the colour centres in the powders from the spectral position of their absorption maxima which is the same as in single crystals. Again, at this stage of investigation, our primary problem is to identify the colour centres and correlate them with the glow peaks in the thermoluminescence curves. Relative changes in the colour centre concentration and half width of the absorption bands are sufficient for this purpose and their absolute values represent a bare statistics. Thus by employing uncoloured NaBr itself as a reference standard, though this statistics is to be sacrificed, the task of interpretation becomes easier as stated below.

At first sight, especially from the shift of the 540 nm band, it may appear that the colouration really has peculiar properties characteristics of the method of colouration. But this shift can be explained in terms of the known interactions of colour centres, mutual and with dislocations which are abundant in powders. Thus such a colouration may be obtained by the other conventional methods under suitable conditions. The important difference between γ ray colouration and discharge colouration is that the former is carried out in a total dark condition, whereas in the latter, a rather intense light produced in discharge as a glow of residual air, is present. This light acts in two ways. It may bleach the F centres to form the F aggregate centres, or the electrons released from F centres may be trapped in dislocation debris. In powders two physically intertwined sub-systems exist (Hersh: private communication): 1. the perfect lattice system which will respond to aggregation process and 2. the imperfections (made up of dislocations, etc.), which bound the indestructible small regions within each crystallite where the latter process will be dominant. In some crystals

dominant aggregation has been observed (Moharil and Deshmukh 1976a). For NaBr, the aggregation is not effective. A possible reason is that there are too many unknown centres around to trap electrons released from *F* centres (Fowler: private communication). Interaction of colour centres with dislocations is now well known (Crawford and Clark 1973). Absorption due to the electrons trapped in debris has been measured for some systems (Hersh and Cocoo 1967). These centres are generally known as *E* centres. During the initial stages of colouration only *F* centres are formed and optical absorption is characteristic of the *F* band and thus peaks occur at 540 nm. After prolonged colouration due to bleaching by the light generated in the discharge itself, electrons are released from *F* centres and trapped in the dislocation debris resulting in the formation of *E* centres. *E* centre absorption is very broad, as if composed of several closely spaced unresolved absorption bands, and usually peaks at the longer wavelength side of the *F* centre absorption maxima. The total absorption due to *F* centres and *E* centres together, thus consisting of two bands, one peaking at 540 nm (due to *F* centres) and the other at the longer wavelengths, will be broad and peak at the wavelengths longer than 540 nm, depending on the relative concentrations of these two types of centres. With increased *E* centre concentration and consequently for the longer colouration periods, maxima should continuously shift towards longer wavelengths, as is observed experimentally. The process continues till an optical equilibrium is reached between *F* centre concentration and *E* centre concentration. Absorption maxima at 590 nm should correspond to this case and should be close to *E* centre absorption maxima.

Such an explanation seems quite sound but one can still doubt whether the formation of *F* aggregate centres would also result in a similar shift. In fact, the visible absorption tails more and more broadly with the increase in the colouration time, which may imply the formation of *M* centres which peak at 820 nm (Jacobs and Menon 1968). However, the *M* centre absorption alone cannot overlap the *F* centre absorption due to such a large difference in the spectral position and cause a shift in the absorption maxima. *R* centres which are expected (Compton and Rabin 1964) to peak at 610 nm and 660 nm might have caused such a shift, but it is known that the first product of bleaching in *M* centre and *R* centre are produced only during the later stages of bleaching. From the fact that there is no resolved absorption peak near 820 nm it is clear that the *M* centres, if formed at all, have a small concentration and so the possibility of *R* centre formation is ruled out. The only plausible explanation involving dislocations is the one given above. This, however, implies that in a perfect (undeformed) single crystal such a phenomenon should not occur. At least it has not yet been reported. It is also not yet clear as to why the external bleaching cannot simulate the same effect. Probably, during the external bleaching, *E* centres are not formed and electrons are destroyed by recombination instead. Perhaps, simultaneous colouration and bleaching is necessary in powders to produce the bleaching products. Such an experiment for the colouration by ionizing radiations has not been reported to date.

Thermoluminescence glow curves can also be explained by a similar reasoning. The peak at 390°K, appearing invariably at all the glow curves, corresponds to *F* centres. Kink at 335°K may correspond to *F* centres formed during the initial stages of colouration. Another peak at 480°K, as it is enhanced by the increase in the colouration time and consequently increased *E* centre concentration, is related to deformational effects. This is consistent with the fact that this grows with the shift in the

absorption maxima. During the isothermal bleaching electrons are released from *F* centres and transferred to *E* centres, enhancing the glow peak at 480°K.

In conclusion, it appears that at least in the powder form NaBr, lattice does not respond appreciably to aggregation. After all these years of research on the *F* aggregate centres in alkali halides we are still unable to answer as to why some of the alkali halides like NaF possess abnormally high M/F ratios whereas others like NaBr are infinitesimally small.

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