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# Reflectance spectra and thermoluminescence of NaF coloured in an electrodeless discharge

S V MOHARIL and B T DESHMUKH
Department of Physics, Nagpur University, Nagpur 440010

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**Abstract.** A comparative study of $\gamma$-ray colouration and electrodeless discharge excitation is reported for NaF. New absorption bands and glow peaks were found. These are shown to be characteristic of electrodeless discharge method of colouration. These are attributed to the multiple types of defects. Further, it is shown that the process by which such defects are formed is strongly temperature dependant. A tentative explanation for the peculiar characteristic of the electrodeless discharge excitation is put forth. The possibility of exploiting these peculiarities for the study of certain properties of colour centres is pointed out.

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

## 1. Introduction

It is known that paramagnetism and colour centres can be induced in alkali halides excited by a Tesla discharge. Samples treated in an a.c. corona discharge are known to emit light pulses (Westermark 1960). Following these initial experiments alkali halides were coloured in an electrodeless discharge to avoid the contamination from the metal electrodes and their properties were studied. (Arnikar *et al* 1971). It was noted that this method of colouration has got peculiar characteristics of its own over other conventional methods of colouration. Thus rapid bleaching of the alkali halides coloured in this method was noted and some new bands were observed in aquoluminescence spectra. Even superficial observations revealed the difference in the behaviour of the samples coloured by this method. However, the nature of this difference is not well understood and even precise experimental description is lacking. Detailed study regarding the nature of the defects produced in an electrodeless discharge and further peculiarities of this method of colouration was undertaken in this department. Results of these studies will be reported in this and subsequent papers.

In this paper we report the difference in thermoluminescent and optical behaviour of NaF coloured by this method as compared to that coloured by the $\gamma$ irradiation. Further it is shown that this difference is well correlated. New absorption bands characteristic of this method of colouration, their preliminary study and their generic relation with peaks in the thermoluminescence glow curve is reported. The possibility of exploiting the peculiarities of this method for the study of certain properties of colour centres is pointed out.

## 2. Experimental details

Experimental set up for an electrodeless discharge is described elsewhere (Arnikar *et al* 1971, Mande and Kanitkar 1970). Analar grade NaF in fine powder form, from Reanal Hungary, was used without further purification, and measurements were restricted to powdered samples. Single crystals were not grown. Two samples were coloured in an electrodeless discharge, one at — 10° C and another at room temperature (20° C) each for an hour. Carl Zeiss spark generator $HFO_2$ was used as a power supply of 12 kv (eff.) 0·45 MHz. Another sample was coloured by exposing to $\gamma$ rays from $^{60}Co$ source for dose of $10^4$ R at room temperature. This sample was used to prove that the peculiar properties of the samples are characteristic of the method of colouration and not of the impurity therein. Immediately after, the colouration reflectance measurements were made at room temperature, against the reflecting surface freshly prepared out of NaF from the same source. Reflectance measurements were made on Carl Zeiss spectrophotometer VSU–2P with 45/0 geometry in the range 280 nm–700 nm. The experimental set-up for recording the glow curves is also described in literature (Jain and Mahendru 1965, Kathuria 1974). Thermoluminescence measurements were made in the range 25° C to 350° C, using a photomultiplier with a S 20 response and uniform heating rate of 25° /M.

## 3. Results

Figure 1 shows the results of the reflectance measurements on the coloured samples in the range 280–700 nm. For the sake of comparing the spectra with conventional absorption spectra, log 100/R, instead of R, the reflectance, was plotted against the wavelength. Absorption at 341 nm and 505 nm are the common

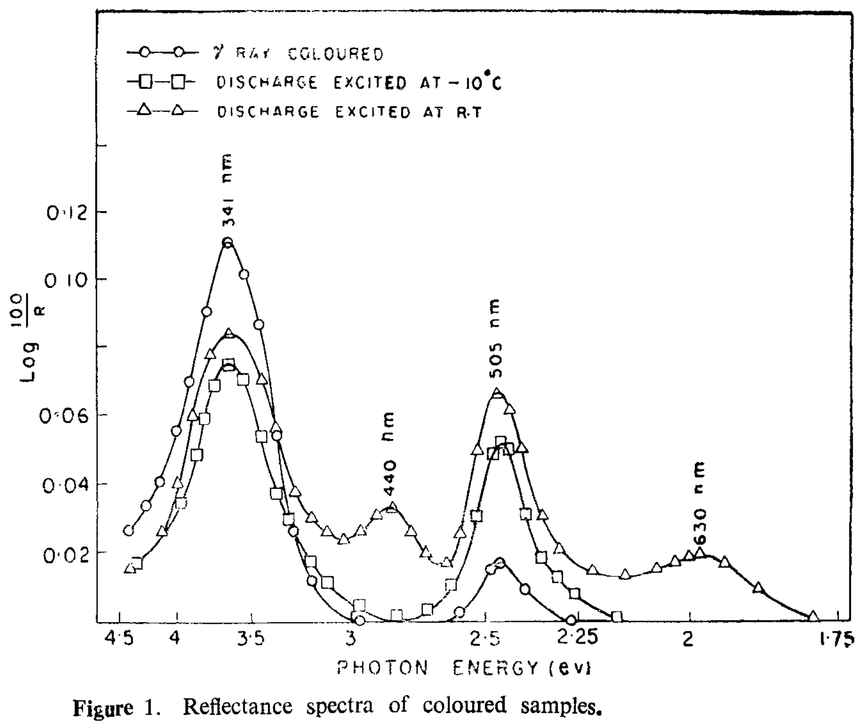


Figure 1. Reflectance spectra of coloured samples.

features of all curves and correspond to F and M centres respectively. Irradiation is known to produce hole centres also but these are not revealed in reflectance curves as they are located in the wavelengths shorter than 280 nm. It is seen that in discharge excited samples, M centres responsible for the absorption peaking at 505 nm, are present in large concentration. The ratio M/F is rather high and inspite of this R bands are not present. In $\gamma$ irradiated NaF the M centre concentration is moderate, M/F ratio being 0·16. A greater half width accompanies the higher M/F ratios in discharge excited samples. Sample excited at room temperature possesses two additional, small but well resolved, absorption bands peaking at 440 nm and 630 nm. These peaks are not present in the sample coloured at — 10° C. Again though the irradiated sample is coloured at room temperature, these two peaks do not occur in its reflectance spectrum. Thus, these peaks cannot be attributed to any impurity present in our sample but seem to be characteristic of the mode of excitation. At present, however, their origin is unknown. From their spectral position it seems that these correspond to electron excess colour centres but it is clear from the same that these are not the R bands which peak at 381 and 415 nm (Compton and Rabin 1964).

Figure 2 shows the glow curves corrected for thermal radiation at higher temperatures. These are equally instructive. Three peaks appearing at 125° C, 220° C and 275° C can be well distinguished in glow curve of $\gamma$ irradiated NaF. Besides these, there is a plateau centred near 50° C. In both of the discharge excited samples all these peaks are shifted towards right. Peak at 125° C is considerably reduced in magnitude and shifted to 137° C, and initial emission at 50° C is completely suppressed whereas the prominent peak at 275° C is enhanced and appears at 300° C and 310° C respectively for the samples excited at — 10° C and room

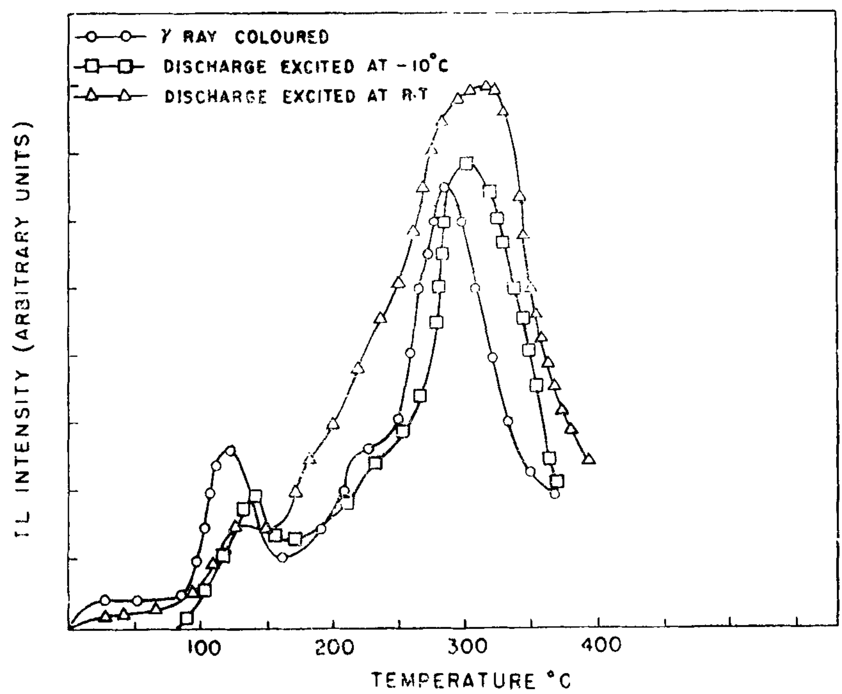


**Figure. 2** Thermoluminescence curves of coloured samples.

temperature. Rising portion of the glow curve corresponding to the sample excited at room temperature is not smooth. Particularly, additional humps occur at 175° C and 240° C. In general this curve envelopes other two curves, though no peak is observed beyond 310° C. This additional emission, most probably, is due to the colour centres responsible for the optical absorption at 440 and 630 nm.

## 4. Discussion

Limitations of the specular reflection are already discussed (Buxton and Duley 1974). However if the method is not useful to determine the parameters like oscillator strength, half width, etc., it can be used to identify the colour centres at least. Further, a comparative study of the half-widths may be justified if not their absolute values. In fact, values for half-width of the F and M centres, 0·69 eV and 0·13 eV respectively, as determined by our method agree closely with literature values 0·71 eV and 0·16 eV (as quoted by Compton and Rabin 1964). Thus it is established that besides F and M centres there are other types of defects, at present unidentified, produced by this method of irradiation. The process by which these are formed is strongly temperature dependant and is completely suppressed at —10° C. Further these defects are responsible for the thermoluminescence peaking at 175° C and 240° C. Detailed analysis of the glow curves regarding the trapping parameters was not undertaken in view of the complicated spectrum observed. Besides, such analysis is not at all necessary for the purpose of correlating the glow peaks with colour centres.

Though the distinguishing features of this method of colouration are rather clear, the root cause for these is not so. Perhaps the main reason for such a difference is that in this method of excitation strong light, ranging from ultraviolet to infrared is produced and thus colouration and bleaching takes place side by side. This may be the reason for high centre concentration. Ultraviolet light is also known to destroy the R bands (Ueta and Hirai 1959). The situation of simultaneous colouration and bleaching, though interesting, is not studied theoretically. Probably this, at room temperature, leads to the formation of multiple types of defects, which result in the shift of glow peaks from their conventional positions and the appearance of new absorption bands in the visible part of the spectra. High electric field also may be responsible for the composite nature of the defects.

Another interesting fact is that, in spite of the high M centre concentration, no R centres are formed in a detectable concentration. If this is characteristic of this method of colouration, then it can be utilized along with the high M/F ratios attainable by this method to study the properties of the M centre that are marred by other electron excess centres. Thus, though the excited states of M centres are established, direct study of these states becomes difficult due to the low concentrations of M centres. With excessive bleaching, R centres are created which complicate the matter. Such difficulties can be encountered by producing adequate M centre concentrations without creating R centres using electrodeless discharge colouration. Experiments in this direction are in progress in this laboratory and will be reported later.

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