

Fluorescence Spectra of Lightly and Heavily Doped $\text{NH}_4\text{Cl}:\text{Tl}$

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The excitation and emission spectra of pure and thallium activated ammonium chloride have been examined at room temperature. It is found that excitation bands at 242 and 256 nm and emission bands at 380 and 460 as well as 500 nm are characteristics of lightly and heavily doped $\text{NH}_4\text{Cl}:\text{Tl}$, respectively. It is suggested that internal electronic transitions in TlCl molecules and $(\text{TlCl}_n)^-$ complex ions are responsible for the two emission band groups.

The thallium doped alkali halides $\text{NaCl}:\text{Tl}$ and $\text{KCl}:\text{Tl}$ have been investigated in great detail [1–7]. Less is known about the excitation and emission spectra of the ammonium halides. The main purpose of the present paper is to examine the fluorescence characteristics of lightly and heavily doped $\text{NH}_4\text{Cl}:\text{Tl}$ phosphors. Attempts have also been made to suggest fluorescence centres for the emissions observed.

Analar grade ammonium chloride powder was obtained from the BDH laboratory, Chemical Division, Glaxo Laboratories, India. Crystallization from aqueous solution was used to prepare microcrystalline $\text{NH}_4\text{Cl}:\text{Tl}$ samples of concentrations 10^{-4} and 10^{-1} m.f. of impurity thallium. The excitation and emission spectra were recorded at room temperature by means of an Aminco-Bowman Spectrophotofluorometer supplied by the American Instrument Co. Inc.

Typical excitation and corresponding emission spectra of pure NH_4Cl and $\text{NH}_4\text{Cl}:\text{Tl}$ specimens with 10^{-4} m.f. and 10^{-1} m.f. of impurities are shown in Fig. 1A and 1B. A comparison of the spectra of pure NH_4Cl , lightly and heavily doped $\text{NH}_4\text{Cl}:\text{Tl}$ specimens brings about the following features:

- (i) Introduction of thallium impurity enhances the fluorescence substantially.

- (ii) The lightly doped $\text{NH}_4\text{Cl}:\text{Tl}$ (10^{-4} m.f. $\geq \text{Tl}$), specimen displays a dominant excitation band at 242 nm with a corresponding emission peak at 380 nm.
- (iii) The excitation band at 242 nm shifts to 246 nm in heavily doped $\text{NH}_4\text{Cl}:\text{Tl}$ (10^{-1} m.f.). The corresponding emission exhibits a new emission in the visible region around 460 nm along with the dominant one at 380 nm.
- (iv) The most striking feature of the heavily doped $\text{NH}_4\text{Cl}:\text{Tl}$ specimen is the appearance of an additional well defined excitation band around 256 nm with corresponding emissions at around 460 and 500 nm. The emission at 380 nm appears as hump.

According to present understanding the luminescent centres comprise of an emitter (inherently present or deliberately introduced impurity) and a

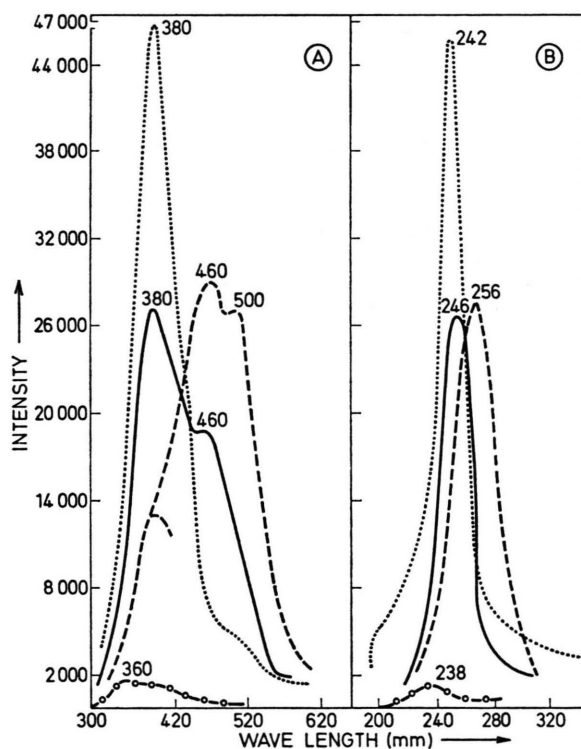


Fig. 1. (A) Emission Spectra, (B) Corresponding excitation spectra. —○—○—○— pure NH_4Cl , lightly doped $\text{NH}_4\text{Cl}:\text{Tl}$ (Tl concentration 10^{-4} m.f.), — and ---- heavily doped $\text{NH}_4\text{Cl}:\text{Tl}$ (10^{-1} m.f. of Tl impurity) for near ultraviolet and visible emissions, respectively.

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trapping site (a point defect in the host lattice). The electron-hole recombination at the emitter without multiple trapping leads to the temperature independent spontaneous emission known as fluorescence. Thus we suppose that the luminescence emission is characteristic of the impurity irrespective of host lattice. It is believed that doping of NH_4Cl with thallium generates a large number of isolated Tl^+ ions, TlCl molecules and $(\text{TlCl}_n)^-$ complexes whose relative concentrations depend on the concentration of the thallium impurity. The introduction of 10^{-4} m.f. of Tl impurity in NH_4Cl causes the prominent 380 nm emission band on 242 nm excitation (Figure 1). As it has been reported that the emissions around 320 nm and 380 nm are associated with Tl^+ ions and TlCl molecules, respectively [3, 7], it is suggested that, like in Tl-activated alkali halides, internal electronic transitions in undissociated TlCl molecules are mainly responsible for the 242 nm excitation and corresponding 380 nm emission in the case of lightly doped $\text{NH}_4\text{Cl}:\text{Tl}$. The mechanism of fluorescence suggested for this emission is an excitation induced electron transfer from

a halide ion (Cl^-) to a neighbouring Tl^+ ion and recombination with it.

It is further suggested that increasing concentrations of thallium create substantial amounts of $(\text{TlCl}_n)^-$ complex ions along with TlCl molecules, influencing the TlCl molecules and causing the shift in the 242 nm excitation band to 246 nm (Figure 1B). On the other hand, the heavily doped specimens should display new emissions associated with the $(\text{TlCl}_n)^-$ complex ions themselves. The appearance of the 460 and 500 nm emissions along with the dominant 380 nm emission strengthens this expectation. Figure 1 (dashed lines) demonstrates the favourable excitation band at 256 nm for the 460 and 500 nm visible emissions. It is proposed from the present experimental results that both the TlCl molecule and $(\text{TlCl}_n)^-$ complex ions are present in $\text{NH}_4\text{Cl}:\text{Tl}$ phosphor and that internal electronic transitions in the complex ions $(\text{TlCl}_n)^-$ are mainly responsible for the visible emissions. The fluorescence mechanism for the visible emission is more or less similar to that suggested for the 380 nm emission.

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