Phosphorescence Decay in Thallium-Doped Ammonium Chloride

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The phosphorescence decay rates of thallium-doped ammonium chloride (NH_4Cl:Tl) phosphors, prepared by crystallization from aqueous solution, have been studied at room temperature for near-ultraviolet emission. The effects of impurity concentration as well as thermal and/or mechanical treatment on the decay rates have been examined. Phosphorescence centres consisting of a Tl^+ion and a nearby negative ion vacancy are suggested to be responsible for the observed luminescence decay. The changes in the decay characteristics after pretreatments are explained on the basis of the location of the centres in normal and distorted regions of the host lattice.

Phosphorescence decay rates of thallium doped phosphors involving alkali halides as base material have extensively been studied [1–3]. A detailed study of the luminescent decay behaviour of thallium activated ammonium chloride has not been reported so far. The present work was therefore undertaken to examine the effect of various pretreatments on the decay rates of NH_4Cl:Tl phosphors.

The work was carried out with polycrystalline specimens crystallized from aqueous solutions of four different impurity contents. The host and incorporated impurity materials were reagent grade ammonium chloride and thallium chloride, respectively. One batch of the specimens so prepared was annealed and quanched from 450 K. Another batch was thermally treated as above and subsequently subjected to deformation by stressing. The decay curves were recorded using an Aminco-Bowman spectrophotofluorometer. In all the experiments, the specimens were excited at room temperature with radiation around 200 nm from a Xenon lamp, and the corresponding phosphorescence was measured for emission in the near-ultraviolet region.

The phosphorescence decay rates of NH_4Cl:Tl phosphors containing various amounts of Thallium, in as-obtained and thermally and/or mechanically pretreated conditions are presented in Figure 1. The notable features are: (i) the intensity of the luminescence is significant in lightly-doped specimens and very weak in heavily-doped specimens, (ii) the phosphorescence decay comprises more than three components, and (iii) in all the cases the mechanical treatment reduces the number of decay components to two.

The suggestion made by Vannotti et al. [4] from their optical absorption results on pure and thallium doped ammonium chloride and the comparison of the present luminescence decay behaviour of NH_4Cl:Tl with that of Tl-activated alkali halides lead one to believe that the optical properties of NH_4Cl:Tl correspond closely to those exhibited by thallium-doped alkali halide phosphors. Following earlier hypothesis [2, 3], it is therefore suggested that neighbouring substitutional Tl^+ ions (emission centre) and negative ion vacancies (trapping site) form the phosphorescence centres responsible for the observed luminescent decay. The after-glow is suggested to be due to the recombination of the electron trapped at a negative ion vacancy with the adjacent parent Tl^+ ion by a tunnelling process. As suggested in the case of Tl-activated alkali halides, it is presumed that in lightly-doped NH_4Cl:Tl phosphors isolated Tl^+ ions are more numerous than in havily doped ones, due to the formation of Tl^+ ion pairs or higher aggregates. As a results, the ultraviolet emission, attributable to single or isolated Tl^+ ions, reduces in intensity as is obvious from the figure (curves 1, 2, 3, and 4). It is further observed that prior to mechanical treatment the decay curves consist of three or more than three independent components. The environment in which the phosphorescence centre is situated would significantly influence the decay rate. Based on this premise, it is suggested that the three or more components of the decay are due to different distances between the phosphorescent centres and the dislocations inherently present in the microcrystals. Deforming the specimens by stressing will involve dislocation motion and multiplication during which some of the phosphorescent centres may act as pinning sites for the dislocations. There will then be phosphorescent centres either in the dislocationfree regions or closely situated near dislocations. Such a situation will give rise to two components for the decay of the deformed specimen. The thermal treatment does not seem to have noticeable effect on the decay characteristics of the phosphors. Thermal quenching from higher temperatures was

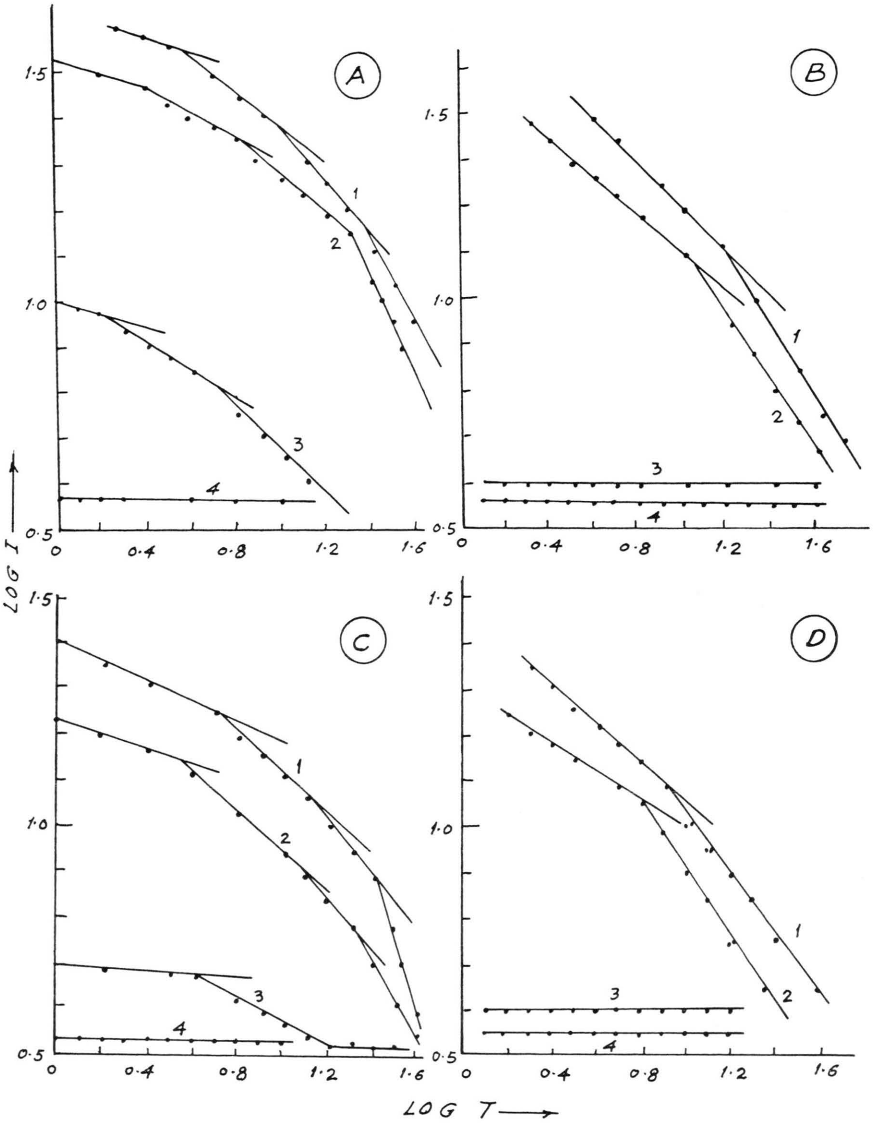

Fig. 1. Room temperature phosphorescence decay curves for $NH_4Cl:Tl$ phosphors. Curves 1, 2, 3 and 4 correspond respectively to specimens with Tl concentrations 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} m.f. A) as-obtained; B) as-obtained and pressed to tablet; C) thermally treated; D) thermally treated and then pressed to tablet.

not possible because NH_4Cl decomposes around 500 K. Under this condition, the thermal strains produced in the specimens may not be sufficient to induce an increase in the dislocation density of the crystal and hence the decay characteristics mainly remain unchanged.

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