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Luminescence of undoped sodium chloride.

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Pure sodium chloride, quenched rapidly from high temperatures, yields a pronounced excitation band at 260 nm which induces a prominent emission band at 360 nm. It is suggested that these bands are characteristic of the centres involving oxygen and ion–vacancy interactions in the NaCl lattice.

The present work concerns the investigation of the nature of the centres responsible for luminescence in heat-pretreated undoped sodium chloride. One specimen batch was annealed at 500 °C in evacuated and sealed tubes and quenched rapidly to room temperature (quenched *in vacuo*). Another specimen batch was quenched rapidly to room temperature in a platinum crucible after annealing at 500 °C (quenched in air). In yet another pretreatment, NaCl:Sr specimens prepared from aqueous solution with 10^{-4} *M* Sr content were annealed in evacuated and sealed tubes and quenched rapidly to room temperature after annealing at 500 °C. All the specimens were annealed for a duration of 50 h. In all cases the excitation and emission measurements were carried out with powder specimens on a Aminco–Bowman spectrophotofluorometer. Area of the sample exposed to the exciting radiation, geometry of the experimental arrangement, *etc.* remained unaltered throughout the course of the experiments. The luminescence output was recorded on Honeywell strip-chart recorder.

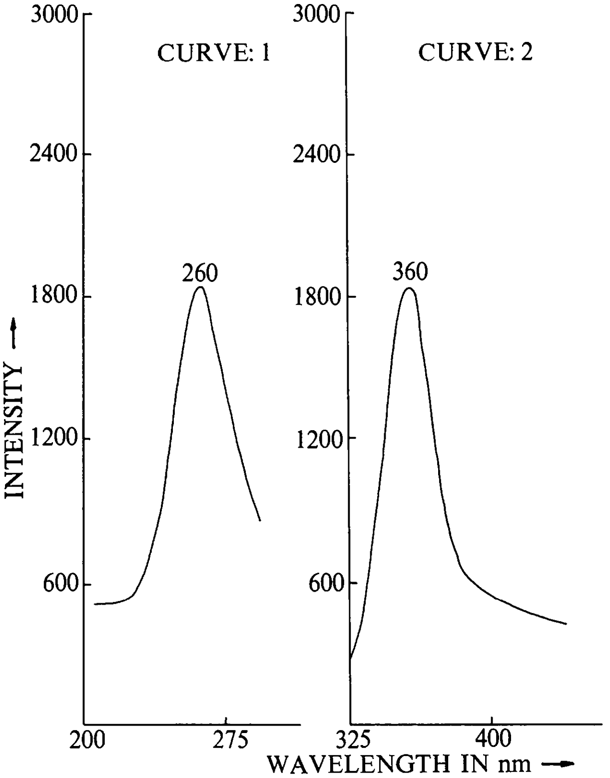

Fig. 1. Excitation (curve 1) and emission (curve 2) spectra of undoped NaCl powder annealed in an evacuated and sealed tube at 500 °C for 50 h and quenched rapidly to room temperature.

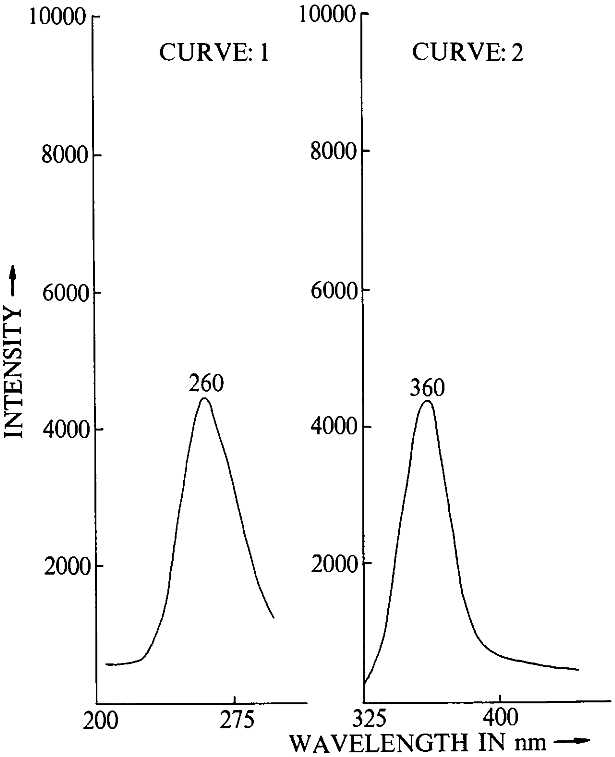

Fig. 2. Excitation (curve 1) and emission (curve 2) spectra of undoped NaCl powder annealed in air at 500 °C for 50 h and quenched rapidly to room temperature.

The excitation and emission data presented in Figs. 1 and 2 relate to the thermally treated undoped NaCl powder specimens. It is obvious from these figures that the excitation spectra consist of a single dominant band at 260 nm and the emission spectra induced by this excitation display a prominent band at 360 nm. It is worth noting that the excitation and emission bands are favoured if the heat treatment is carried out in air instead of in an evacuated and sealed tube (compare Figs. 1 and 2).

It is suggested that the heat-treated undoped NaCl specimens acquire the property of becoming luminescent because the surface of a microcrystal (in the powder specimen) exposed to air becomes activated owing to adsorbed gases. Apparently the activating impurity, presumably O_2^+ molecule-ions or O_2 neutral molecules, is incorporated in the surface of the microcrystal. At a given temperature the attack on the surface layers by oxygen molecules will naturally depend on the air pressure. The pressure in the evacuated and sealed tubes in the present experiments was of the order of 10^{-3} mm of Hg. This explains the difference in the luminescence intensity of the two specimens, one heated *in vacuo* and the other in air (Figs. 1 and 2) though both were annealed at at 500 °C for the same duration. It is believed, therefore, that an oxygen molecule-ion O_2^+ or a neutral molecule O_2 situated on a cation site is one of the components of the luminescence centre responsible for 260 nm excitation and 360 nm emission.

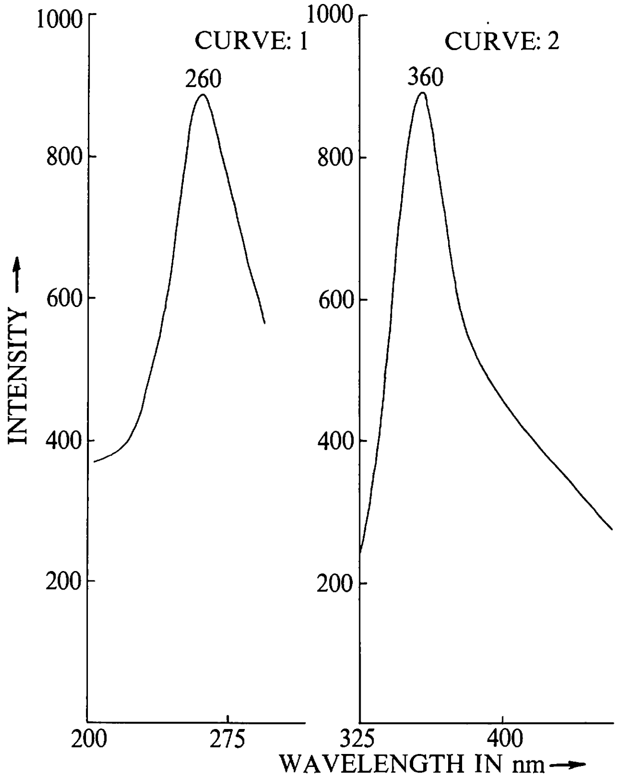

Fig. 3. Excitation (curve 1) and emission (curve 2) spectra of a NaCl : Sr powder specimen prepared from aqueous solution (Sr concentration 10^{-4} *M*). Specimen annealed and quenched in an evacuated and sealed tube at 500 °C for 50 h and quenched rapidly to room temperature.

Comparison of the intensities of the excitation and emission bands displayed by an undoped NaCl specimen, annealed and quenched from 500 °C *in vacuo*, with the intensities of the corresponding bands exhibited by a doped NaCl specimen (Sr concentration 10^{-4} *M*) also annealed and quenched from 500 °C *in vacuo*, clearly demonstrates that the introduction of a trace amount of strontium impurity suppresses the intensities of the luminescence bands by a factor of about 2·5 (compare Figs. 1 and 3). It is known that a major fraction of the divalent impurity ions incorporated in an alkali halide crystal become associated with positive-ion vacancies forming impurity–vacancy dipoles and their higher aggregates (Cook & Dryden, 1960, 1962; Dryden, 1963). It therefore seems plausible that the positive-ion vacancies produced by quenching are used up in the generation of dipoles and this inhibits the formation of 360 nm centres. It is not possible to specify the exact composition of the 360 nm centre. It may involve the O_2 molecule or O_2^+ molecule-ion in association with one or more positive-ion vacancies.

It may be mentioned that oxygen has been suggested as a common impurity of most of the 'pure' alkali halides, though of course, little definitive work has been done with this impurity (Kanzig & Cohen, 1959; Schulman & Compton, 1963). Halperin, Kristianpoller & Ben-zvi (1959) attributed the thermoluminescent emission of undoped alkali halides to centres composed of oxygen impurity and ion vacancies.

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A different best rigid-body molecular fit routine*.

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A different algorithm which gives a least-squares fit between two sets of atoms is described [*cf.* Nyburg (1974). *Acta Cryst.* B**30**, 251–253]. With this algorithm the coordinates of the moving set of atoms are changed only once.

Rigid-body least-squares best molecular fit programs have recently been described by Nyburg (1974) and by Gavuzzo, Pagliuca, Pavel & Quagliata (1972). We routinely use a different method for obtaining the best fit. This method has been incorporated into the system of programs *REFINE*2 developed in this laboratory for model building (= idealization, if desired with nonbonded energy constraints) and conformational analysis primarily of protein molecules (Hermans & McQueen, 1974; Hermans, Ferro, McQueen & Wei, 1976: these Fortran programs are available upon re-

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