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Fig. 1

Figure 1: Fig. 1

Abstract

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PREPARATION OF ALKALI-HALIDE CRYSTAL PHOSPHORS BY THE METHOD OF SURFACE TREATMENT

(Presented by Academician A. V. Shubnikov, 28 I 1969)

In work (^{1}) it was shown that surface treatment of photochemically and additively colored KCl and NaCl single crystals with an aqueous solution of silver nitrate, after appropriate annealing, leads to the formation of various silver centers, manifested in the absorption spectrum of these crystals as characteristic bands. Apparently, such treatment leads to the appearance in the surface layer of the crystals of silver ions which, by capturing electrons released during the destruction of F-centers, form silver centers. The detection of such centers, similar to what was observed for alkali-halide phosphors activated with silver and grown from the melt (^{2}), gave grounds for assuming that surface treatment of crystals with solutions of salts of metals whose cations are sufficiently isomorphous with the host can lead to the formation of distinctive crystal phosphors.

In the present communication we present the results of a study of KCl and NaCl crystals treated with solutions of thallium nitrate and copper sulfate.

A few drops of an aqueous solution of $TlNO_3$ ($C = 0.03$ g/ml) were applied to one of the faces of freshly cleaved crystals measuring $15 \times 10 \times 2$ mm. The concentration of the solution was chosen so that the treatment could conveniently be carried out several times. The crystals were then dried in air, annealed at 650° for one hour, and rapidly quenched to room temperature, after which the spectral distribution of their absorption (on an SF-4 spectrophotometer) and luminescence (on a photoelectric photometer) was measured. The results obtained are shown in Fig. 1A.

Fig. 1. Absorption spectra (1, 2) and luminescence spectra (3, 4) of alkali-halide

crystals treated with solutions of $TlNO_3$ (A) and $CuSO_4$ (B); 1, 4 –KCl, 2, 3 –NaCl.

In the absorption spectrum, well-defined bands are observed with a maximum near 245 mμ for KCl + $TlNO_3$ crystals and near 255 mμ for NaCl + $TlNO_3$. With an increase in the amount of applied solution, the intensity of these bands increases, but without any noticeable change in their spectral position. The emission spectra are characterized by bands with maxima at 290 and 305 mμ for NaCl + $TlNO_3$ and KCl + $TlNO_3$ crystals, respectively. Measurements of the excitation spectra, carried out according to the method described in (^{3}), showed the presence of bands whose maxima coincide with the maxima of the absorption bands.

In a number of cases, after two- or threefold treatment with the solution, in a KCl crystal, along with the short-wavelength luminescence band at 305 mμ, it is possible to observe also a broad band with a maximum near 500 mμ. An increase in the intensity of the long-wavelength emission band is accompanied by a decrease in the intensity of the short-wavelength band, and vice versa. This indicates that centers of types I and II are formed, both of which participate in the luminescence (^{4}).

Treatment of crystals with an aqueous solution of copper sulfate ($C = 0.02$ g/ml) was carried out analogously to treatment with a thallium nitrate solution. The fact that, as a result of the reaction occurring on the surface, $CuCl_2$ is formed was not of substantial importance. As shown in (^{5}), where alkali-halide crystals with CuCl and $CuCl_2$ impurities were studied, at high temperatures $CuCl_2$ decomposes into CuCl and Cl_2. Therefore, in such crystals, irrespective of whether they are doped with monovalent or divalent copper, only the band belonging to Cu^+ is always observed.

Figure 1b shows the absorption and luminescence spectra for treatment with a $CuSO_4$ solution. In the absorption spectrum, bands are observed at 255 and 265 mμ for NaCl + $CuSO_4$ and KCl + $CuSO_4$ crystals, respectively; in the luminescence spectra, a band at 355 mμ for NaCl + $CuSO_4$ and at 390 mμ for KCl + $CuSO_4$. The excitation spectra are characterized by bands coinciding with the absorption bands.

A specially conducted study also showed that the anionic impurities formed, NO_3^- and SO_4^{2-}, do not appear in the absorption spectra of the treated crystals in the form of the characteristic bands that were observed in (^{6}).

In order to check the results obtained, crystal phosphors based on KCl and NaCl, activated with Tl (0.2 mol.%) and Cu (0.1 mol.%), were grown by the Kyropoulos method and were studied under the same conditions as the crystals treated with the corresponding solutions. It was found that in both cases practically coincident spectral characteristics are observed, in agreement with the literature data (^{7}, ^{3}). In addition, both activation methods used by us gave phosphors with approximately identical quantum yields. This gives grounds to believe that surface treatment of alkali-halide crystals with solutions of thallium or copper leads to the formation, in the near-surface layer, of solid substitutional solutions. Consequently, the proposed method may be of practical interest.

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Note: Figure translations are in progress. See original paper for figures.