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Neutralization of Hydroxide Ion in Melt-Grown NaCl Crystals

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MANY recent studies of solid-state phenomena, particularly in the area of crystal imperfections, have involved the use of melt-grown NaCl single crystals. Quite often trace impurities in these materials have had a prominent effect on these phenomena. Trace amounts of hydroxide ion have been found in melt-grown NaCl crystals.¹⁻⁴ This paper describes a non-destructive method of neutralizing the hydroxide ion in such crystals. Crystals of similar hydroxide content are maintained at an elevated temperature below the melting point of NaCl in a flowing atmosphere containing dry hydrogen chloride. Heat treatment is continued until an analysis of the test specimens shows no excess hydroxide ion. A colorimetric method previously described⁴ is used for this analysis.

The crystals had a cross section of 4×7 mm and a length of 2 to 4 cm. They were rinsed with four or five portions of carbon tetrachloride or chloroform to remove organic impurities from their surfaces. A platinum boat holding these crystals was placed in a quartz tube inside a tube furnace. The boat had a tightly fitting cover and platinum tubes extending from its sides to the cooler portions of the system in order to retard attack of the quartz by the salt vapors. Glass-wool plugs, previously freed from organic substances by heating to 650°C in an airstream, were used as heat shields inside the system. The apparatus was purged for about 3 or 4 hr with argon to remove the oxygen. Dry hydrogen chloride, prepared by adding concentrated hydrochloric acid to concentrated sulfuric acid, was then passed through the system until the atmosphere in contact with the salt was primarily HCl. The portion of the system containing the NaCl was heated to and

maintained at 730°C for 48 hr in the slowly moving HCl atmosphere.

Failure to remove oxygen from the system permitted reactions that destroyed the boat and the salt wherever they were in contact, deposited platinum on the hot surfaces of the system, deposited a compound thought to be Na₂PtCl₆ on the cooler parts, and produced considerable amounts of free chlorine. When the glass wool or the crystal was not free from organic material, a thin, black, uneven deposit was found on the treated crystals.

When starting with melt-grown crystals of NaCl having an initial concentration of 20 ppm or less, treatments of 48 hr reduced the NaOH concentration in these crystals to less than 1 ppm. All Optovac OH-free and Harshaw crystals tested at this laboratory initially contained 20 ppm NaOH or less. However, neutralization was incomplete in all crystals containing hydroxide that were treated only 24 hr and in some crystals initially containing more than 20 ppm NaOH even with the 48-hr treatment. The times involved suggest that a solid-state diffusion mechanism is involved in the neutralization.

Additional experiments have also shown that hydroxide ion can be reintroduced into neutral crystals by heating them in an atmosphere of argon and water vapor at 730°C for 2 hr. Furthermore it may be possible to introduce other anion impurities by treatment of crystals containing hydroxide ion in atmospheres of the corresponding acid.

¹ J. Rolfe, *Phys. Rev. Letters* **1**, 56 (1958).

² H. W. Etzel and D. A. Patterson, *Phys. Rev.* **112**, 1112 (1959).

³ W. H. Etzel and J. G. Allard, *Phys. Rev. Letters* **2**, 452 (1959).

⁴ D. A. Otterson, *J. Chem. Phys.* **33**, 227 (1960).