

1.5 Crystal Growth and Properties of Nonlinear Optical Derivatives of Benzaldehyde Phenylhydrazone and DAST

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One of the derivatives of benzaldehyde phenylhydrazone, 4-dimethylaminobenzaldehyde-4-nitrophenyl- hydrazone (DANPH) and one of the stilbazolium salts, 4'-dimethylamino-N-methyl-4-silbazolum tosylate (DAST) are two interesting new candidates for nonlinear optical and electro-optic application. Larger bulk size crystals with good optical quality are needed to measure their nonlinear optical and electro-optic properties and to use them as optical devices. Difficulties in growing these types of crystals, which contain highly polar molecules with donor- and acceptor groups bridged by double aromatic rings bearing double bonds, are:

(1) Thermal unsuitability of crystals at the melting point limits the growth techniques. Therefore solution growth method at low temperature is often the only possibility.

(2) In solution, polymorphism, which can always occur in different solvents and kinetic processes of crystal growth, can complicate the growth condition.

(3) Crystal growth in solution always shows typical characteristics, e.g. thin plates or needles, since a strong polar anisotropy of these molecules produces special intermolecular interactions with polar or H-bond solvents along various orientations of the growth faces of the crystals.

Features of DANPH are that : (1) there exist two phases of black and red colour, of which only the black form is nonlinear optically active, (2) in polar and H-bond solvents the black form can only be crystallised in a fast cooling process; otherwise, in slow cooling or evaporation, the red form is easily produced, (3) the solvent, acetonitrile, is the best for growing the black form, in which triangular, thin, small (010) plates are produced. Some crystals with maximum dimensions up to 15 mm x 6 mm x 2 mm carefully prepared from large, thin seed crystals. The main problem for growing DANPH is the decomposition and polymerisation that occurs in the growth solution when exposed to light, heat and low concentrations of water in the solvent and the environment. Therefore the growth solution can only be used for a short period and the growth faces are roughened by the generated impurities.

Features of DAST are that : (1) there exists a hydrated phase of orange colour, that is nonlinear optically inactive and a phase of black colour that is highly nonlinear optically active; (2) the habit form grown in methanol (the best solvent for its growth), is a thin (001) plate, (3) the twinning growth occurs easily when developing the growth along the crystal thickness. By carefully preparing the seed crystal and controlling the supersaturation to develop the facets, crystals of good optical quality checked by polarized microscopy, with maximum dimensions up to 16 mm x 16 mm x 3 mm were obtained.

Further work on DANPH and DAST includes (1) the preparation of samples of good optical quality by cutting and polishing of the crystals and further measuring their nonlinear optical and electro-optic properties; (2) growing more large crystals of even better quality, and (3) investigating their growth mechanism.