

1.7 Polymorphism, Growth and Properties of Organic Nonlinear Optical Crystals

(F. Pan, M.-S. Wong and Ch. Bosshard)

The growth of large single crystals of excellent quality are a pre-requisite for optical and nonlinear optical investigations as well as for future applications. As discussed below polymorphism (different crystalline structures for one molecule) is one of the problems that has to be solved in order to grow bulk crystals. All materials described here were most successfully grown from solution.

We found that most derivatives of push-pull phenylhydrazones showed a polymorphic behaviour. Interestingly, forms showing high SHG efficiency have been found in these derivatives by varying the growth conditions and the solvents of crystallisation. Two promising materials, 4-dimethylaminobenzaldehyde-4-nitrophenyl-hydrazone (DANPH) and 5-(methyl-thio)thiophene-carboxaldehyde-4-nitrophenylhydrazone (MTTNPH) were grown for optical measurements. DANPH (form II) was investigated by using different growth techniques: solution growth (in the solvent CH₃CN), gel growth, and physical vapor transport growth. With these methods bulk crystals (20×10×1 mm³) very thin plates (10×5×0.05 mm³), and films (2×2 mm² in area with a thickness of about 0.01~0.05 mm) were grown, respectively. In addition, large size bulk crystals of MTTNPH (25×5×5 mm³) with good optical quality were grown from CH₃CN solution.

For the first time, high quality large size DAST crystals up to 20×20×5 mm³ were grown from methanol solution successfully. Polarized microscopic studies showed a homogeneous extinction between crossed polarizers confirming the good optical quality of our samples. This is a major breakthrough since DAST is the material with the largest second-order nonlinearities in the wavelength range of 700-2000nm.

The co-crystal, 4-{2-[1-(2-hydroxyethyl)-4-pyridylidene]ethylidene}-cyclo-hexa-2,5-dien-1-one · methyl 2,4-dihydroxybenzoate (Mero-MDB) crystallizes in two different forms. Mero-MDB (form I) with the merocyanine dye in complete parallel alignment in the co-crystal (ideal for electro-optic applications) was grown in methanol up to a size of 3×2.5×2.5 mm³ with good optical quality. Mero-MDB (form II) crystallizes centrosymmetrically. In this case, the merocyanine dye and methyl 2,4-dihydroxybenzoate are aligned in a complete anti-parallel fashion in the co-crystal. For the study of third-order nonlinear optical properties crystals of the form II are grown from methanol.