

**o.m1.o1** Crystal engineering of organic-inorganic materials for quadratic nonlinear optics. R. Masse, *Laboratoire de Cristallographie, CNRS, BP166, 38042 Grenoble Cedex 09, France*

Keywords: herringbone motif, nonlinear optics, hydrogen bond.

Well known inorganic crystals as KDP, BBO, KTP,... and isotypes have reached a high level of development in laser applications mainly due to high mechanical and thermal stabilities associated to a large transparency range (0.3 to 3  $\mu\text{m}$ ) and nonlinear optical efficiencies from 0.2 to 3pm/V. Molecular crystals built-up with organic chromophores having remarkable hyperpolarisabilities as 3-methyl-4-nitroaniline (MNA), 4-nitrophenyl-L-prolinol (NPP), 3-methyl-4-methoxynitrostilbene (MMONS),... revealed high nonlinear optical efficiencies from 10 to 100pm/V. Although their engineering be more tailor-made than that of inorganic crystals these NLO molecular crystals have not had until now an impact in laser applications due to their poor mechanical and thermal stabilities. In order to improve the stabilities of these organic materials and save their high NLO efficiencies for future optical devices we have developed since 1991 a crystal engineering strategy in which the organic chromophores are hosted in inorganic networks. Numerous non-centrosymmetric crystals have been synthesized with the 2-amino-5-nitropyridinium as typical chromophore. For this chromophore, we have evidenced through many crystal structures a geometrical rule which allowed to predict new non-centrosymmetric crystal packings. Then we have used a typical anionic chromophore as nonlinear entity, the 4-nitrophenolate ( $\beta_{\text{xxx}} = 18 \text{ to } 23 \cdot 10^{-30}$  esu), for a crystal engineering route of organic salts, coordination compounds and molecular complexes. We will show the wealth of the non-centrosymmetric structures built with these chromophores and their derivatives, the importance of the bond strengths which induce the crystal packing, the role played by the inorganic network in crystal stability and nonlinear hyperpolarisabilities. The structures contain herringbone motifs of polar chromophores often close of the ideal packing, a situation for which the maximum contribution of  $\beta_{\text{ijk}}$  to the macroscopic tensorial coefficients is realized. Crystals including multidipolar or octupolar chromophores also engineered with success will be presented. An optical parametric oscillator has been realized with the crystal of 2-amino-5-nitropyridinium dihydrogenphosphate the performances of which justify this crystal engineering.

**o.m1.o2** Photorefractivity of  $\text{Sn}_2\text{P}_2\text{S}_6$ . S. Odoulov, A. Shume-lyuk, S. Pavlyuk, and D. Barilov. *Institute of Physics, National Academy of Sciences, 03 650, Kiev, Ukraine.*

Keywords: photorefraction, four-wave mixing, phase conjugation.

Tin hypotiodiphosphate ( $\text{Sn}_2\text{P}_2\text{S}_6$ , SPS) is a ferroelectric photorefractive material [1], suitable for all applications involving the recording of the refractive index grating (coherent light amplification, phase conjugation and laser beam clean-up, image processing, holographic interferometry, etc.) Its photorefractive sensitivity covers the range from the band edge (about 2.3 eV) till at least 0.9 eV. The largest electrooptic coefficient is  $r_{111} \geq 100$  pm/V. We report on characterization of the crystal by means of nonlinear optical spectroscopy and on implementation of various frequency degenerate four-wave interactions in this material. The crystals are grown in the Institute of Solid State Physics and Chemistry, Uzhgorod State University, Ukraine.

It is supposed that main charge transport process involved in grating formation is via photoinduced charge hopping. Two types of movable charge carriers are involved in grating formation that leads to partial compensation of the ultimate grating in the steady state. The parameters like the Debye screening length and diffusion length of the photoexcited carriers, effective trap density, dark- and photo-conductivity and the hierarchy of the linear electrooptic coefficients are evaluated.

A special emphasis is given to unusually fast space-charge relaxation in SPS (milliseconds and below) when compared with the standard wide bandgap photorefractive crystals like  $\text{BaTiO}_3$  or  $\text{LiNbO}_3$ .

A second part of the talk is devoted to nonlinear interactions in SPS and to techniques that might improve the efficiency of the four wave mixing. We present the results on nearly frequency degenerate wave mixing [2], on the use of the active feedback for grating recording, on the recording at the reduced temperature. The application of the external DC field of the order of 2000 V/cm allows for the inversion of the sample spontaneous polarization and, consequently, for the inversion of the beam coupling direction. At the same time such a field improves considerably the gain factor that can reach  $15 \text{ cm}^{-1}$  in the near-infrared region of spectrum.

[1] Odoulov S., Shumelyuk A., Hellwig U., Rupp R., Grabar A., and Stoyka I. "Photorefraction in Tin Hypotiodiphosphate in the Near-Infrared", *J. Opt. Soc. Am. B*, (1996), 13 : 2352-2360.

[2] Shumelyuk A., Odoulov S., and Brost G. "Multiline coherent oscillation in photorefractive crystals with two species of movable carriers", *Appl. Phys. B*, (1999), 68 : 959-966.