



ESRF

Experiment title: X-RAY TOPOGRAPHY OF PROMISING NONLINEAR OPTICAL CRYSTALS: THE 2-AMINO-5-NITROPYRIDINIUM ORGANIC SALTS

Experiment number: HC-534

Beamline: D5 - ID19	Date of experiment: from: 01/02/96 to: 31/12/96	Date of report: 01/03/97
Shifts: 3	Local contact(s): BARUCHEL J.	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

- A. IBANEZ*, Lab. Cristallographie, CNRS Grenoble
- J. ZACCARO*, Lab. Cristallographie, CNRS Grenoble
- E. PRIEUR*, ESRF, Grenoble.
- J. ESPESO*, ESRF, Grenoble.
- R. MASSE*, Lab Cristallographie, CNRS Grenoble.

Report:

We have undertaken in 1994, at the lab. Cristallographie, CNRS-Grenoble, the crystal growth in solution of a new type of promising materials for nonlinear optical (NLO) applications. These hybrid organic-inorganic phases try to combine the advantages of organic crystals (high NLO efficiency) and mineral materials (good stability, wide transparency range) [1-3]. Large (several cm³) and optically clear crystals have been grown for the 2-amino-5nitropyridinium salts as chloride (2A5NPCl), phosphate (2ASNPDP), arsenate (2ASNPDA_s) and those of the 2ASNPDP(1-x)As_x (0<x<1) solid solution. Their crystalline quality has been then characterized by X-ray topography.

The preliminary X-ray topographic tests, carried out at ESRF D5 Optics beamline were then completed by a topography study realized on ID'19 in collaboration with J. Baruchel, E. Prieur and J. Espeso. The first experiments have shown that these organic-inorganic NLO crystals are stable under the illumination of the high energy X-rays. The low energies of the white beam is filtered away and the remaining high energetic part of the beam (energies from about 15 to 80 keV) do not create thermal effects in the crystal which is a serious problem when working with a synchrotron radiation with low energies. Due to the long penetration length of high energetic photons also the thick crystals could be studied so that the grown crystals have not to be thinned. Thus, as shown in figure 1, clear X-ray topographs are obtained from a thick 2A5NPCl crystals.

The figure 1 was taken by a section topography method which is a very useful technique because it allows to probe thick crystal plates without any slicing (all these organic-inorganic crystals have not easy cleavage plane). Correlations between topography results and growth conditions have allowed to improve significantly the crystalline quality of the 2A5NPCl (figure 2) [4], 2A5NPDP and 2A5NPDA's [5] salts. The determination of the best experimental growth conditions for the 2A5NPDP(1-x)Asx ($0 < x < 1$) crystal is under development.

These crystals are now optically characterized in collaboration with the lab. Spectrometrie Physique, UJF-Grenoble leading to correlations between the crystal quality and linear optical properties (absorption, scattering, damage threshold...). Moreover, the results arising from X-ray topography as the nature of defects or as the densities of dislocations can be related to the values of the non-linear optical tensorial coefficients.



Fig.1: X-ray section topograph of 2A5NPCl crystal ($1 \times 1.5 \times 2 \text{ cm}^3$) demonstrating, among other things, dislocations propagating from the seed (up left). Magnification 13X



Fig.2: X-ray section topograph of a high quality 2A5NPCl crystal showing a low density of dislocations far from the seed which is down left.

References

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- [2] Y. Le Fur, M. Bagieu-Beucher, R. Masse, J.F. Nicoud, J.P. Levy, submitted to *Chem. Mater.*, 8 (1996) 68.
- [3] French Patents: 9014743, 9304116 and 9205077 currently extended to USA, Japan and EEC.
- [4] A. Ibanez, J.P. Levy, C. Mouget and E. Prieur, *J. Solid State Chem. in press* (1997).
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