15-Crystal Growth

was performed in powdered Li_2CO_3 at 500°C for 24 hours. The colour of the sample is light red after reduction, and transparent before. Absorption spectra were taken at room temperature. An absorption peak appears clearly at 500 nm in the spectrum of the reduced sample. It is due to an F centre, a defect related to a forbidden oxygen vacancy with two electrons, V_o^{2}. The absorption side of the reduced sample shifts towards longer wavelengths because the concentration of Nb atoms which occupy Li sites in the crystal, Nb_{Li}^{4}, has increased.

Phase analysis was made by X-ray diffraction at room temperature. No other new phases were formed during the reduction process. The lattice parameters were calculated by means of the least square method. The value of *a* decreases slightly from 5.1486 Å to 5.1482 Å, and that of *c* increases slightly from 13.8304 Å to 13.8420 Å.

Because the reduction temperature is 500°C, the reduction process is believed to be due to the diffusion and the movement of Li^+ ions which have a small size, but not to O atoms diffusing from the host crystal. The latter case needs a high temperature and an oxygen-lacking atmosphere. A possible mechanism is thought to be:

$$LiNbO_3 + (V_{Nb}^{5}, Nb_{Li}^{4}) \leftrightarrow 3/2\ O_2 + Li^+ + \dot{N}bNb + Nb_{Li}^{4} + 6\ e^-$$

In this case, oxygen is liberated from the crystal during the reduction and there remains an oxygen vacancy, V_o^{2-}, at the original place, together with a Nb_{Li}^{4} which has been formed. Otherwise, the complex defect $(V_{Nb}^{5}, Nb_{Li}^{4})$ in the congruent $LiNbO_3$ partly disappears during the reduction.

In $LiNbO_3$, Li^+ and Nb^{5+} ions are surrounded by distorted octahedra of six O^{2-} ions. The cations sit between the planes containing triangles of O^{2-} ions, Nb being at the centre of an octahedron, and Li more off-centre. During the reduction described above, as the Li^+ ions are liberated from the host crystal by diffusion, the plane of O^{2-} ions triangles contracts slightly, and the lattice constant *a* becomes slightly smaller. On the other hand, because Nb^{5+} combines with V_{Nb}^{5} to form $\dot{N}b_{Nb}$, the triangle of O^{2-} which is nearest to V_{Nb}^{5} gets larger, and the lattice constant *c* gets larger as well.

** Supported by the Foundation of Natural Science of China

PS-15.02.13 STUDY ON GROWTH CHARACTERIZATION OF L-ARGININE PHOSPHATE MONOHYDRATE.

By Aidong Li, Shenman Guo, Hongxi Zhang* and Chongquan Xu, Department of Applied Chemistry, Harbin Institute of Technology, HARBIN 150006, P.R. China.

L-Arginine phosphate monohydrate (LAP) is a promising nonlinear optical organic crystal for higher threshold and harmonic generation in place of the conventional KDP in the LASER fusion programme. In this paper, the results of our recent investigations on its growth by slow cooling are presented. It was found that the orientation and fixing method of LAP seeds had a great influence on the renewal period of LAP crystal morphology. In order to obtain good seeds, the secondary-seed technique was adopted. The microbe-pollution and coloration of the LAP solution were the main factors affecting the optical quality and the growth habit of LAP crystals. A new inhibitor-liquid paraffin was found to have a better effect because it overcame the short durability of H_2O_2 and the easy evaporation, coloration and inconvenience of n-hexane. Coloration of the solution could be avoided by keeping the growth temperature low and preventing it from microbes. It was experimentally shown that LAP crystal growth was controlled by the interface reaction. The negative *b*-axis is especially sensitive to the impurities formed by the thermal and microbe decompositions of L-arginine. In ambient light, the photo-induced decomposition of L-arginine was neglected. By slower cooling at a rate of 0.10 to 0.15 °C/day from 40°C to 30°C, high-quality LAP crystals as large as 1*1*2 cm^3 were obtained. Their damage-threshold at 1064 nm was higher than 20 GW/cm^2.s.

In conclusion, the experimental results indicated that the quality of the seed, the purity of the solution and the proper supersaturation were the keys for growing perfect LAP crystals.

PS-15.02.14 CRYSTAL GROWTH AND STRUCTURE OF TOLANE NONLINEAR OPTICAL MATERIALS.

By Chaoguo Wang, Congxuan Yu and Jinseng Feng*, Beijing Institute of Technology, China.

A novel tolane 4-methoxy-4'-nitro-diphenyl-acetylene (MONA) has been prepared quantitatively by reaching Cuprous p-methoxy phenyl-acetylene with p-iodonitrobenzene. It is one of series 4-methoxy-4'-nitrodiphenyl- diacetylene (MONDA) and 3-methyl-4-methoxy-4'-nitrostilbene (MMONS), which have been synthesized in our laboratory. A single crystals of the MONA was grown by solution growth method. The crystal was characterized by X-ray diffraction structure analysis and SHG investigated. We found that three morphology differences for crystals of the MONA grown from difference solvent. In this lecture we report our work on crystal growth and crystal structure of the 4-methoxy-4'-nitrodiphenylacetylene (MONA). We also observe that polymorphological growing crystal from different solvents and its difference of the THG properties. The α-MONA is a centrosymmetric. Its crystal structure is triclinic, with space group P -1, a=11.912(3), b=12.110(3), c=14.818(4) A, α=99.53(2), β=113.02(2), γ=92.81(2), $V=1924.76A^3$, Z=6, $Dx=1.311g/cm^3$.

The structure was solved by direct method (MULTAN 82) from data collected at room temperature on an Enral-Nonius CAD4 diffractometer and refined by least squares to a final R value of 0.077 using 1900 reflections. In this molecule structure show plane structure and strangle bond in this plane. The presence of planer faces on a crystal may be taken to indicate growth by z layer mechanism. The most prominent faces, which are the slowest growing, tend to have a predominance of strong bonding within the grown layer results from the difficulty of starting or nucleating a new layer on account of the weak bonds holding it to the preexisting surface. The crystal growth is entirely dependent on the structure. α-, β-, γ-MONA phases have been compared by X-ray powder diffraction data, and their SHG effect was evaluated. δ-MONA (raw material) is only possessed of SHG active. The existence of polymorphism adds complication to the crystal growing process but also introduces flexibility. To understand these complicated polymorphs and their effects on the nonlinear optical and photophysical properties, large single crystals of these compounds must be grown and their structures determined. At present we have structure informations on α-MONA, which was grown from ethyl-acetane solution having a centrosymmetric structure (triclince P -1). It doesn't possibility nonlinear optical properties. We suggest that use 'Crystal engineering' designed molecule with hydrogen bond and with hand group formed uncetronsymmetry structure.