

## 15-Crystal Growth

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PS-15.02.09 CRYSTAL GROWTH AND DEFECT OBSERVATION OF  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> AND LiB<sub>3</sub>O<sub>5</sub> SINGLE CRYSTALS. By J.K. Kang, C.H. Kim, B.M. Lim, and S.J. Chung\*, Department of Inorganic Materials Engineering, Seoul National University, Seoul 151-742, Korea.

Single crystals of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO) and LiB<sub>3</sub>O<sub>5</sub> (LBO) have been grown by top-seeded solution growth using fluxes of Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub>, respectively. (Chen, C.T., J. Crystal Growth, 1990, 99, 790-798) These flux systems cause many problems on crystal growth, such as a high solution viscosity, low growth rate, and a high defect concentration. So, these fluxes were modified by adding fluorides. BBO crystals up to 75x75x15mm<sup>3</sup> in size could be grown at a cooling rate of 2~10°C/day, seed rotation rate of 2~10 rpm, and pulling rate of 0.2~1mm/day, and LBO crystals 20x20x10mm<sup>3</sup> in size, at 1~3°C/day, 5~20 rpm, and 0.1~0.3 mm/day.

During the crystal growth, inclusions such as bubbles and fluxes were usually concentrated around the seed crystal, and the cellular structure was generated at a high growth rate. Thermal strain and thermal shock caused the development of dislocation bundles and cracks in the growing crystals. These grown-in defects were investigated by X-ray topography, optical microscopy and electron microscopy. We have studied the change in morphology according to flux modification and the relationships between the generation of defects and growth conditions.

PS-15.02.10 GROWTH, CHARACTERIZATION AND PROPERTIES OF MIXED Nd-La HEPTAMOLYBDATE CRYSTALS. By Sushma Bhat and P.N. Kotru, Department of Physics, Jammu University, J&K, INDIA, M.L. Koul, Department of Chemistry, Jammu University, J&K, INDIA, R.P. Tandon, NPL, New Delhi, INDIA. Growth of single crystals of mixed Nd-La heptamolybdates in silica gels is achieved using single gel as well as double gel techniques. Seeded growth and concentration programming enhances the ultimate size of crystals. Data on the characterization of these crystals employing XRD, TEM and IR (structural characterization), EDAX (chemical characterization) and optical and scanning electron microscopy (morphological characterization) are reported and discussed. The thermal stability of the crystals is investigated employing TG, DTA and DSC. It is estimated that the crystals carry 35 waters of hydration which renders them thermally unstable at slightly above room temperatures (>40°C). The study shows that there are no phase transitions as such. Solid state reaction kinetics are studied using Piloyan-Novikova, Coats-Redfern and Horowitz-Metzger and Barret's equations. The data yielding the values of frequency factor, activation energy, and order of reaction are presented. Pallets of 2.5 mm thickness and 7.2 mm diameter are used for dielectric measurements employing LF 4192 Impedance Analyser. Dependence of Dielectric constant and loss (tan  $\delta$ ) on temperature and frequency is investigated. The dielectric constant increases as the temperature is increased, attains the maximum value and then decreases steadily; the maximum value of  $\tan \delta$  depends on the frequency. The detailed data is presented and discussed.

PS-15.02.11

THE GROWTH OF Mg<sub>2</sub>Fe<sub>2</sub>LiNbO<sub>3</sub> CRYSTAL AND THE MEASUREMENTS OF EXPONENTIAL GAIN COEFFICIENT\*\*. By Zhao Yequan\* Li Ming hua, Gao Yuankai, and Xu Yuheng, Department of Applied Chemistry, Harbin Institute of Technology, Liu Jinghe, Department of Material Engineering, Changchun Institute of Optical Machinery, P. R. China.

It has been shown that the ability of resistant photorefraction and photorefractive sensibility of LiNbO<sub>3</sub> crystals can be enhanced by doping them with MgO and Fe<sub>2</sub>O<sub>3</sub>. Its two-wave mixing gain (103cm<sup>-1</sup>) is four times that of BaTiO<sub>3</sub> and the response rate of phase-conjugation was increased by an order of magnitude.

The Mg<sub>2</sub>Fe<sub>2</sub>LiNbO<sub>3</sub> crystals were grown by using Czochraski technique. The components of the melt are Li<sub>2</sub>CO<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>=48.6/51.4 (mole ratio), 5 mole% MgO and 0.08mole% Fe<sub>2</sub>O<sub>3</sub>. In order to grow perfect crystals, the optimum growth conditions that we have used are as follows: axial temperature gradient 40°C/cm, growth rate 2-3mm/h, rotation rate of the crystal 20-30 rpm. Then, the crystals were polarized so as to become single domain crystals by passing through them 5mA/cm<sup>2</sup> of current density at 1220°C. For multiple memories, the concentration of [Fe<sup>3+</sup>] should be very larger than that of [Fe<sup>2+</sup>] so as to reduce erasion during memory, therefore, Mg<sub>2</sub>Fe<sub>2</sub>LN should be oxidated in Nb<sub>2</sub>O<sub>5</sub> powder at 1000°C for 10h and reduced in Li<sub>2</sub>CO<sub>3</sub> powder at 500°C for 40h for read-write memory application. Furthermore, we have measured the visible-infrared absorption spectra and OH<sup>-</sup> extensive oscillation transmitting spectra of the crystals. There is a small peak (2cm<sup>-1</sup>) at 490nm for the oxidated crystal; and a big peak (15cm<sup>-1</sup>) at 480nm for the reduced crystal; the transmitting spectra present two absorption peaks at 2830nm and 2850nm respectively. And the former is more higher than the latter. Finally, we have also measured the two wave mixing gain, the results is 103cm<sup>-1</sup>, when  $\beta=1049$ ,  $2\theta=11.5^\circ$ .

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PS-15.02.12 REDUCTION OF PHOTOREFRACTIVE LiNbO<sub>3</sub> CRYSTALS IN POWDERED Li<sub>2</sub>CO<sub>3</sub>. By Li Minghua\*, Gao Yuanquan, Zhao Yequan and Xu Yuheng, Department of Applied Chemistry, Harbin Institute of Technology, P.R. China.

Reduction is an effective way to enhance the photorefractive sensitivity of LiNbO<sub>3</sub> crystals. One kind of reduction occurs at temperatures higher than 1000°C, in vacuum or in an Ar atmosphere. The reduction mechanism is attributed to oxygen atoms liberated from the host crystal at high temperature. In 1974, W. Phillips and D.L. Staebler found that LiNbO<sub>3</sub> packed in powdered Li<sub>2</sub>CO<sub>3</sub> at 500°C or so may be reduced more completely. In the present paper, this reduction process is investigated by using absorption spectra and X-ray diffraction. A congruent LiNbO<sub>3</sub> crystal was grown by the Czochralski method. Reduction of the crystal

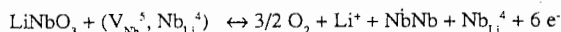
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was performed in powdered  $\text{Li}_2\text{CO}_3$  at 500°C for 24 hours. The colour of the sample is light red after reduction, and transparent before.

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,  $\text{Nb}_{\text{Li}}^{4+}$ , 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  $\text{Li}^+$  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:



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  $\text{Nb}_{\text{Li}}^{4+}$  which has been formed. Otherwise, the complex defect ( $V_{\text{Nb}}^{5-}, \text{Nb}_{\text{Li}}^{4+}$ ) in the congruent  $\text{LiNbO}_3$  partly disappears during the reduction.

In  $\text{LiNbO}_3$ ,  $\text{Li}^+$  and  $\text{Nb}^{5+}$  ions are surrounded by distorted octahedra of six  $\text{O}^{2-}$  ions. The cations sit between the planes containing triangles of  $\text{O}^{2-}$  ions, Nb being at the centre of an octahedron, and Li more off-centre. During the reduction described above, as the  $\text{Li}^+$  ions are liberated from the host crystal by diffusion, the plane of  $\text{O}^{2-}$  ions triangles contracts slightly, and the lattice constant  $a$  becomes slightly smaller. On the other hand, because  $\text{Nb}^{5+}$  combines with  $V_{\text{Nb}}^{5-}$  to form  $\text{Nb}_{\text{Nb}}$ , the triangle of  $\text{O}^{2-}$  which is nearest to  $V_{\text{Nb}}^{5-}$  gets larger, and the lattice constant  $c$  gets larger as well.

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**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  $\text{H}_2\text{O}_2$  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<sup>3</sup> were obtained. Their damage-threshold at 1064 nm was higher than 20 GW/cm<sup>2</sup>.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 reacting 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  $\alpha$ -MONA is a centrosymmetric. Its crystal structure is triclinic, with space group P -1,  $a=11.912(3)$ ,  $b=12.110(3)$ ,  $c=14.818(4)$  Å,  $\alpha=99.53(2)$ ,  $\beta=113.02(2)$ ,  $\gamma=92.81(2)$ ,  $V=1924.76$  Å<sup>3</sup>,  $Z=6$ ,  $D_x=1.311$  g/cm<sup>3</sup>. The structure was solved by direct method (MULTAN 82) from data collected at room temperature on an Enraf-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.  $\alpha$ -,  $\beta$ -,  $\gamma$ -MONA phases have been compared by X-ray powder diffraction data, and their SHG effect was evaluated.  $\delta$ -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  $\alpha$ -MONA, which was grown from ethyl-acetane solution having a centrosymmetric structure (triclinic 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 uncentrosymmetry structure.