15-Crystal Growth

PS-15.02.15 HOW CAN WE SOLVE PROBLEMS OF CRYSTAL GROWTH OF ORGANIC NLO MATERIALS ?-SELECTION OF METHODS, TEMPERATURE AND SOLVENTS FOR ORGANIC NLO CRYSTAL GROWTH. By Chaoguo Wang, Beijing Institute of Technology, China

High quality organic crystals are needed for X- ray diffraction structure analyses and for use as nonlinear optical devices. Current routine and nonroutine methods of growing organic crystals are discussed and the influence of temperature and organic solvents on the character of organic NLO crystal was examined experimentally. Growing method and conditions of MONA, MONDA, MMONS, NMDA, POM according to their physical and chemical properties are made and those are more suitable for organic NLO materials. In actual practice a growth method can not give suitable for difference organic crystals. Alternatives of growth method are according to the crystal chemistry and properties of the particular compound. Several examples from our recent research work serve to illustrate this point. The organic NLO materials have usually hyperpolar molecule, but most typical organic solvents are a dipole moment less than about 3 Debye. Therefore, The ideal solubility and similar dipole solvent is difficulty selected to growing large three-dimensional crystals can be expected to grow in the solution. The nonpolar solvents tend to form lowly dimensional crystal, and a polar solvents favors formation of bulk crystals. Many organic compounds usually melt below 200 ℃ and char at high temperature. Proposal of growing method is selected by thermal example DSC and optical request. As crystal growth practitioners we know that the art of crystal growth is much more highly developed than the science much work need to be done to improve existing methods for organic crystal preparation. The effort needs to be interdisciplinary involving organic chemists, crystallographers and materials scientists. As scientists, we believe that crystal growth mechanisms are rational and ultimately under- standable. Innovative, interdisciplinary approaches are needed to make advances in this field, and the future utility of organic solid as technologically important materials depends on such advances(Author, G. Zhang et al., J. of Crystal Growth 1990, 100, 411-415).

PS-15.02.16 **THE STUDY ON A NEW ACOUSTO-OPTIC MATERIAL---LEAD BROMIDE CRYSTAL.** By Chen Fusheng, Institute of Crystal Materials, Shandong University, Jinan 250100, China

Lead bromide crystal has become a very important Acousto-Optic (AO) material because of its excellent AO performance. A new Acoustic-Optic Tunable Filter (AOTF) made from the crystal has been used to fabricate Infrared Spectrometers which has been found wide applications.

Using directional crucible decreasing method, larger size up to φ20 * 60mm, colorless, transparnent lead bromide single crystal was grown, the growth rate is 1-2cm/day. Crystal growth experiments indicated that the orientation of seed crystal, G/V value (G: temperature gradient, V: decreasing rate) and the material purity were the major factors influencing the crystal quality. The appropriate G/V value ranged from 10 to 20, under this condition the solid -liquid interface appeared as a slightly convex or flat faces. Using [001] oriented seed crystal, it's easier to grow nearly perfect crystal, or the cracks will be serious in the grown crystal. The raw material purity should be higher than 99.999% to assure less scattering grains and better uniformity in the crystal.

The transmission range of the grown lead bromide crystal extends from 0.4 to 30 μm. X-ray powder diffraction pattern and Laue photography indicated the lead bromide belongs to mmm point group. The crystal defects and their causes were also studied.

PS-15.02.17 INVESTIGATIONS OF CONTROLLED REVERSION OF SOLID-LIQUID INTERFACE DURING GROWTH OF YAG:Nd CRYSTALS. By Xu Tianhua, Peng Weiqing, Zheng Qimeng, Huang Changmin and Xu Guangyu, Southwest Institute of Technical Physics, PO Box 238, Chengdu 610041, P.R. China.

There are four clearly differentiated states of liquid flows that can be found in various combinations of diameters and rotation rates of the crystals, namely, I. simple natural convection; II. coexistence of natural and forced convections with an asymmetric overcooling region caused by the "window effect"; III. coexistence of the same liquid flows but without that region and IV. simple forced convection. In general, states I and III last long, while state II is short; state IV occurs when the diameter of the crystal is large in comparison with the inner diameter of the crucible and when the difference in temperature is relatively small between the crystal and the crucible. In all mentioned transitions, namely, I → II, II → III and III → IV, abrupt changes in the diameter of the crystal and remelting of the growth interface to a certain extent were observed. Component supercooling and generation of dislocations occur frequently.

It is obviously undesirable to grow the crystals in states II and III. In order to grow in state III, it is necessary for the crystals to go through states I and II and two rapid transition processes which cause component supercooling and generate dislocations. In this connection, we have developed a method called "Contolled Reversion of Solid-LiquidInterface" (CRSLI), which allows the growth to go into state III immediately after a dislocation-free top has grown during state I, and thus to obtain crystals free from dislocations. The key to realize the "safe" transition from I to III is: 1. choosing a suitable position; 2. setting-up of a suitable thermal field; 3. keeping the crystal growth in a stable liquid flow rate; 4; not having the residue of the region of unstable growth appearing inevitably during the interface reversion.

When crystals are grown following this procedure, the growth process as a whole is not continuous in space and time, and thus has broken the normal procedure.

PS-15.02.18 COMPARISON OF THE GROWTH OF YAG:Nd CRYSTALS IN RESISTANCE AND RF HEATING SYSTEMS. By Xu Tianhua, Peng Weiqing, Zheng Qimeng, Huang Changmin and Xu Guangyu, Southwest Institute of Technical Physics, PO Box 238, Chengdu 610041, P.R. China.

We have grown YAG:Nd crystals in a graphite heating molybdenum crucible and in an RF heating iridium crucible, separately, and found that there is an appreciable distinction between them in the growth conditions (atmosphere, thermal field and liquid flow behaviours), the growth parameter control (stability of the diameter, permissible growth rate and doping level), as well as in the results on the growth of the crystal (external shape, surface morphology and absorption spectrum).

In the first case, when filled with argon (nitrogen cannot be used), the furnace was in a reductive atmosphere, the surface of the crystal was severely contaminated due to an interaction between graphite, molybdenum and the constituents of the crystal, and the crystal had an absorption peak near 3700 Å. In the second case, the furnace was in a neutral atmosphere (Ar and/or N_2), and the crystal had a wide absorption peak near 2600 Å. The above mentioned peaks can be eliminated by a long-term atmospheric annealing at a temperature ranging from 1200 to 1300°C. With regard to the setting-up of the thermal field, the first case usually shows a larger (or more suitable) regulating range of the longitudinal and radial temperature gradients, as well as a higher doping level and growth rate than in the second case. The doping levels (the atomic ratios in the starting materials) were larger than 5 % and ≈ 4 %, repectively, their pulling rates were 2.0 to ≈ 2.5 mm/hr and 1.0 to ≈ 1.3 mm/hr, respectively. Even in such conditions, the normal crystal/charge ratio for the first case (resistance

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heating) can reach 80 % and more while in the second case (RF heating) it is usually 30 to 40 %. Moreover, in the first case, the state of the liquid flow was easier to control, and, when grown with a flat interface, the crystal had a better diameter stability and its cross-section tended to be quite circular, but the surface finish was very poor (the analysis suggests that this is due to the interaction between volatile compounds from the graphite, the molybdenum and the crystal surface). As a rule, the YAG:Nd crystals grown with the resistance process are most suitable for pulsed devices while those grown using the RF process are mostly used for continuous devices.

PS-15.02.19 DEFECTS IN YAG:Nd CRYSTALS CAUSED BY INTERFACE REVERSION. By Xu Tianhua and Xu Guangyu, Southwest Institute of Technical Physics, PO Box 238, Chengdu 610041, P.R. China.

A region 1 to 2 cm long with macroscopic "filamentary" defects often appears in YAG:Nd crstals when their growth interface undergoes "spontaneous reversion". Microscopic examination has revealed that the region has the typical features of component supercooling: sharp images of cellular growth and interface breakdown appear after etching on the crystals sliced longitudinally; the "filaments" are usually tubular, and many "granules" of a secondary phase which are formed from the melt after climbing are imbedded in their inner walls. The defects due to the component supercooling resulted in two forms of dislocations: prismatic dislocation loops surrounding the filaments which do not extend downwards, and linear and helicoidal dislocations running roughly along the normal to the interface. After etching of the crystals sliced longitudinally, arrays of etch pits were observed on opposing faces with a good correspondence, as well as etch cannelures originating from the ends of the filaments due to the linear dislocations and arrays of etch pits due to the helicoidal dislocations. After etching of the crystals sliced transversally, some closely-packed bursts of dislocation etch-pits were observed surrounding the filaments. In the region where the filaments disappear, there are many scattered dislocation lines decorated with impurities.
The densities of the dislocation etch-pits before and after the region with filamentary defects usually differ from one another by 2 or 3 orders of magnitudes. The facts mentioned above show that the defects due to the component supercooling are the main cause for the generation of dislocations.
Finally, the causes of the defects due to component supercooling as well as their elimination are discussed according to the relationship between the control of the growth parameters, the stability of the liquid flow and that of the interface.

PS-15.02.20 THE THERMAL FIELD IN THE GROWTH OF HIGH TEMPERATURE OXIDE CRYSTALS BY THE CZOCHRALSKI TECHNIQUE. By Xu Tianhua, Peng Weiqing, Zheng Qimeng, Huang Changmin and Xu Guangyu, Southwest Institute of Technical Physics, PO Box 238, Chengdu 610041, P.R. China.

We consider that the thermal fields is the most important factor that affects the pulling in a definite region growth system, and it is mainly characterized by the longitudinal and radial temperature gradients, the symmetry of the temperature gradients, and the smoothness of the variations of the longitudinal temperature gradient. The thermal field strongly affects the morphology and the intensity of the liquid flow, the shape of the interface, the external shape of the crystal, the stability of the crystal diameter, the crystal/charge ratio, the formation of defects, the easines of the operation, and so on.
The larger the temperature gradient, the stronger the natural convection, the more convex the interface, the better the stability of the diameter, and the more the external shape of the crystal tends towards a cylinder, but that will easily lead to cracks in the crystal when it is too large. When the radial symmetry of the temperature distribution is poor (the "cold point" deviates from the centre of the liquid interface), and the crystal is grown with a convex interface, there are a lot of scattered granules in the crystal caused by temperature fluctuations at given points on the growth interface. When the rotation rate is high, poor radial symmetry and a low temperature difference between the crystal and the crucible will result in the appearance of eddies on the surface of the liquid, the stability of the crystal diameter is very poor, and there are a lot of scattered granules in the crystal. When the smoothness of the variations in longitudinal temperature gradient is poor, the crystal has an extremely poor diameter stability which it is difficult to control. Besides, it leads easily to crystal brittleness and to a calabash-shaped growth.
The "window effect" vitally affects all the mentioned characterization parameters. For this reason, we have designed a special device called "Dynamic symmetric forced heat dissipator" in which the liquid flow is in a good state, the crystal/melt ratio is large (up to 60 to 70%), the stability of the diameter is satisfactory, there are no scattered granules, and the control of the growth is facilitated.

PS-15.02.21 GROWTH OF SINGLE DOMAIN NEARLY PERFECT CRYSTALS OF LITHIUM NIOBATE. By R.V. Anantha Murthy*, K.S. Bartwal and Krishan Lal, National Physical Laboratory, New Delhi - 110 012, India.

High quality single crystals of lithium niobate have been grown by the Czochralski technique. A crystal growth system designed, developed and fabricated at NPL has been employed in these experiments. Crystals of diameter 20mm and length 30 mm are being grown. High purity (99.99%) powder was used as the charge. The perfection of the crystals was evaluated by high resolution X-ray diffractometry and topography. The half width of the diffraction curve was in the range 10 arc sec to 20 arc sec (Fig. 1). Also, the topographs reveal that dislocation densities are low. Ferroelectric domains could be observed in X-ray diffraction topographs of the crystals grown without poling. The domains were randomly oriented. Poling during growth experiment was accomplished with current densities in the range 1.5 mA/cm^2 to 2.5 mA/cm^2. These crystals are of single domain and nearly perfect.

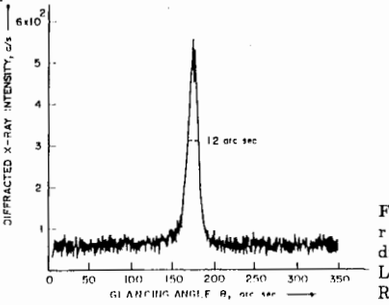

Fig. 1. A high resolution X-ray diffraction curve of a $LiNbO_3$ crystal, $11\bar{2}0$ Relp; MoKα_1; (+,-,+).