

**MS16.03.02 LOW-FREQUENCY VIBRATIONAL CONTROL OF CRYSTAL GROWTH FROM MELT.** E.V. Zharikov<sup>(1,2)</sup>, A.Z. Myaldun<sup>(2)</sup>, A.I. Prostomolotov<sup>(3)</sup>, N.A. Verezub<sup>(3)</sup>, (1)D. Mendeleev University of Chemical Technology of Russia; (2)General Physics Institute of Russian Acad.Sci.; (3)Institute for Problems in Mechanics of Russian Acad.Sci.

Influence of low-frequency (LF) vibrations on growth process and crystal perfection originating from vibrational control of melt flows and heat-mass transfer at crystal growth excite now rising interest of both crystallographers and hydromechanics. The practical importance of forced vibrational convection connected with the fact that the introducing flows allow to influence on crystal quality, to control temperature field, thickness of boundary layer and to suppress temperature oscillations in the melt near the interface by the complex interaction with flows of natural and thermocapillary convections.

Experiments on growth of doped yttrium-scandium-gallium garnet ( $T_m = 2156$  K) by CZ-technique were carried out with applying of LF-vibrations with frequencies and amplitudes preliminary determined by physical modelling of the process. Microprobe analysis of grown crystals shows essential positive effect of the LF-vibrations on crystal perfection. In particular, LF-vibrations can reduce fluctuations of dopant concentration and related striations in the crystal at least by one half. They also can provide flat interface due to strong influence on heat-mass transport processes near the front of crystallization.

**MS16.03.03 LIQUID PHASE EPITAXY OF  $Hf_c$  SUPER-CONDUCTORS.** P. Görnert, T. Aichele, S. Bornmann, C. Dubs, Institut für Physikalische Hochtechnologie e.V., Helmholtzweg 4, PF 100 239, D-07702 Jena, Germany

$YBa_2Cu_3O_{7-x}$  films were grown on (110)  $NdGaO_3$  substrates by liquid phase epitaxy (LPE) using the "step cooling technique". A transition from c-axis to a-axis orientation could be observed with increasing undercooling for different flux melt compositions. Polygonized macrosteps were revealed optically at c-axis films grown at small undercoolings. Atomic force microscopy (AFM) measurements show that macrosteps are composed of a multitude of smaller growth steps. Besides decorated step structures were found on terraced surfaces between the macrosteps. The high quality of epitaxy has been confirmed by X-ray diffraction measurements showing rocking curve widths (FWHM) of  $0.2-0.3^\circ$  for the (005) film reflection. Larger undercoolings of the flux melts result in mixed c/a-axis growth and finally in a-axis growth reported already earlier.

**MS16.03.04 GROWTH AND CHARACTERIZATION OF  $C_{60}$  AND  $C_{70}$  CRYSTALS.** Kenichi Kojima and Masaru Tachibana, Department of Physics, Faculty of Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236, Japan

The success in efficiently synthesizing fullerenes has generated much interest in the physical properties of this new class of molecular crystals. The growth of single crystals with high quality is required for studies on the intrinsic physical properties. In this work,  $C_{60}$  and  $C_{70}$  crystals of large size and high quality were grown from vapor by a continuous pulling technique, and their perfection were examined by X-ray topography and etching method.

$C_{60}$  crystals of small size were used as the source material, which was deposited onto the closed end of a pyrex tube. The tube was evacuated to  $1-3 \times 10^{-6}$  Torr and then sealed off. The tube was placed in a horizontal furnace with two oppositely oriented temperature gradients, where the temperature of the middle portion of the furnace was kept at  $530^\circ\text{C}$  and its opposite sides were at  $580^\circ\text{C}$ . The tube was advanced towards the source at a pulling rate of 1 cm/day in the furnace. After 3-4 days,  $C_{60}$  crystals up to a size of about  $8 \times 4 \times 3$  mm<sup>3</sup> were grown at the middle of the furnace.  $C_{70}$  crystals were also grown in the same way as  $C_{60}$ . Here it was necessary to use higher temperatures of the furnace since the vapor

pressure for  $C_{70}$  is lower than that for  $C_{60}$ .

The perfection of the grown  $C_{60}$  crystals with fcc structures were examined by synchrotron topography. Some of dislocations were individually observed. Most of their Burgers vectors were identified to be  $1/2 \langle 110 \rangle$ . Moreover, dislocation etch pits were observed by immersing the grown  $C_{60}$  crystals into toluene for 5 seconds. From the distribution of the etch pits, the dislocation density in most of the grown crystals was estimated to be less than  $10^4/\text{cm}^2$ .

To make sure of the characteristics of defects, the mechanical properties, such as hardness and plasticity, of  $C_{60}$  and  $C_{70}$  crystals were investigated using the microindentation technique.

**MS16.03.05 CRYSTAL GROWTH AND CHARACTERIZATION OF NLO ACTIVE ORGANIC INCLUSION COMPOUNDS.** Jürg Hulliger, Olaf König, Vera Kramer-Hoss, Institute of Inorg., Analyt. and Physical Chemistry, University of Berne, Switzerland.

Design of efficient organic nonlinear optical (NLO) materials attempts a molecular hyperpolarizability  $\beta_{zzz}$  up to a value close to  $10^7$   $000$   $10^{-40} \text{m}^4/\text{V}$  and seeks for an orientation of  $\beta_{zzz}$  axes that optimizes either frequency doubling (SHG) or the electro-optic (EO) effect of macroscopic crystals [1-3].

On account of a low yield [1-3] of crystal structures providing a parallel alignment of dipoles (max. EO effect), recent interest focused on the packing of NLO molecules along parallel channels of inclusion type lattices [4]. When compared to other host materials [5], perhydrotriphenylene (PHTP) worked out to be ideally suited [6,7] to include a variety of linearly shaped NLO entities of the A- $\pi$ -D type (A, D: acceptor, donor group, respectively;  $\pi$ : thiophene, stilbene, polyphenyl, polyacetylene). SHG powder tests revealed that PHTP-(A- $\pi$ -D) inclusion formation produces polar materials at a yield of around 75% that is 3 times higher than found for corresponding single component systems. Crystals of PHTP-(A- $\pi$ -D) were grown by (i) controlled isothermal evaporation of 2-butanone or paraldehyde, (ii) the temperature difference technique, and (iii) by sublimation [8].

- [1] D S. Chemla, J. Zyss (Eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1,2, Academic Press (1987).
- [2] J. Zyss (Ed.), *Molecular Nonlinear Optics*, Academic Press (1994).
- [3] Ch. Bosshard, K. Sutter, Ph. Pretre, J. Hulliger, M. Florsheimer, P. Kaatz, P. Gunter, *Organic Nonlinear Optical Materials*, Gordon and Breach (1995).
- [4] V. Ramamurthy, D.F. Eaton, *Chem. Mater.*, 6, 1128 (1994).
- [5] E. Weber, *Topics in Current Chemistry*, Vol. 140, Springer (1987).
- [6] J. Hulliger, O. König, R. Hoss, *Adv. Mater.*, 7, 719-721 (1995).
- [7] R. Hoss, O. König, V. Kramer-Hoss, U. Berger, P. Rogin, J. Hulliger, *Angew. Chem.*, submitted.
- [8] J. Hulliger, *Angew. Chem. Int. Ed. Engl.* 33, 143-163 (1994).

**MS16.03.06 GROWTH AND CHARACTERIZATION OF  $(Y,Nd)Al_3(BO_3)_4$  AND  $(Y,Gd)Al_3(BO_3)_4$  CRYSTALS.** Leonyuk, N.I.; Koporulina, E.V.; Belokoneva, E.L.; Titov, Yu.V., Moscow State University, Russia

The crystals of solid solutions based on the  $YAl_3(BO_3)_4$ ,  $NdAl_3(BO_3)_4$  and  $GdAl_3(BO_3)_4$  borates with huntite type structure (R32 space group) are excellent materials for laser and acoustic devices [1,2]. However, the NdAl- and GdAl-borates and their solid solutions tend to the phase transitions from huntite type structure into monoclinic modifications [3]. The purpose of the present work was to establish a correlation between the growth conditions, contents of crystals and phase transitions in  $(Y,Nd)Al_3(BO_3)_4$  and  $(Y,Gd)Al_3(BO_3)_4$  solid solutions.

These crystals were grown from a  $K_2MoO_3O_{10}$ -containing fluxed melts in temperature range  $1060-990^\circ\text{C}$  (spontaneous crystallization) or  $1050-1010^\circ\text{C}$  (TSSG).

The distribution coefficient ( $K=C_s/C_l$ ) was estimated to be

0.3-0.8 for NYAB and about 1 for GYAB crystals. In the case of NYAB it increases with an increase in crystallization temperature and a decrease in the crystal growth rate.

The temperature and concentration ranges of the phase transitions were determined for these crystals by X-ray technique, microprobe analysis, optical and electron microscopy.

#### References

1. L.M.Dorozhkin at all. *Pis'ma v ZhETF*, Vol.7, pp.1297-1299 (1981) (in Russian).
2. L.I.Leonyuk at all. *Acoustoelectronics-89*, Abstr, Varna, Vol.2, pp.459-461 (1989).
3. E.L.Belokoneva at all. *Kristallographia*, Vol.33, pp.1287-1288 (1988) (in Russian)

**MS16.03.07 A NEW FLUX FOR THE RAPID GROWTH OF POTASSIUM TITANYL PHOSPHATE (KTiOPO<sub>4</sub>) SINGLE CRYSTAL.** M. T. Sebastian, S. Suma, N. Santha, Electronic Ceramics Division, Regional Research Laboratory, Thiruvananthapuram-695 019, India

Single crystals of the well known non-linear and electro-optic material KTiOPO<sub>4</sub>(KTP) has been grown using a new barium-potassium based complex phosphate flux. The solubility of KTP in this new flux is higher at high temperatures and low at low temperatures as compared to the conventional flux K<sub>6</sub>P<sub>4</sub>O<sub>13</sub>. The new flux is less viscous and hence avoids the problem of glass formation and a higher cooling rate can be given. Good quality crystals of KTP up to 6mm in size can be grown in a day by giving a cooling rate of 120 °C/day. The KTP crystals grown in this new flux are transparent, free of inclusions or elements from the flux and OH incorporation. The use of this flux indicates the possibility of growing relatively large crystals commercially in a short time.

**MS16.03.08 GROWTH KINETICS OF PROTEIN SINGLE CRYSTALS IN THE GEL ACUPUNCTURE TECHNIQUE.** Abel Moreno<sup>1</sup>, Juan Ma. Garcia-Ruiz<sup>2</sup> & Manuel Soriano-Garcia<sup>1</sup>, <sup>1</sup>Instituto de Quimica-UNAM, C.U. Coyoacan 04510. Mexico, D.F., <sup>2</sup>Instituto Andaluz de Ciencias de la Tierra. C.S.I.C.-Universidad de Granada Campus Fuentenueva s/n 18002 Granada, Spain

This work presents the growth kinetics of protein crystal growth in the gel acupuncture technique. This new method has been proposed previously for the growth of protein single crystals [1]. The main advantage of the technique is that the crystals are obtained inside an X-ray capillary tubes. The growth of single crystals of lysozyme (HEW), Thaumatin within capillary tubes was monitored by time-lapse videomicroscopy. The crystals were obtained by diffusive transport of precipitating agent through capillaries of internal diameter ranging from 0.2 mm to 1.5 mm, using the gel acupuncture technique. For crystals growing from true protein solutions, the measured average growth rates varies with capillary diameter from 2.7 Å/s to 3.7 Å/s for thaumatin and from 2.8 Å/s to 22 Å/s for lysozyme. The measured average growth rates, for crystals growing into gelled protein solutions, were 1.8 Å/s for thaumatin and 2.5 Å/s for lysozyme. In all the cases, the trend in variation of the growth rate with time is similar and suggest that, for capillaries with internal diameter radius lower than 1.2 mm, protein crystals grow in gel and free solution under diffusive mass transport control. Finally, it is showed that the crystal growth rate depends on the height of the capillary tube where nucleation occurs and it is function of the internal diameter of the capillary tube.

Reference:1. Moreno, A. Ph. D. Thesis, Universidad de Granada, Spain. (1995).

**MS16.03.09 HYDROTHERMAL GROWTH AND TWINNING OF GALLIUM PHOSPHATE CRYSTALS.** O.V.Zvereva and L.N.Demianets, Institute of Crystallography, RAN, Moscow, Russia

Modified hydrothermal method was developed for gallium orthophosphate single crystal growing. The concentrated mixture of phosphonic acids with the boiling temperature of 225°C was used as a growth media. Crystals were grown in the field of positive temperature coefficient of solubility (T>300°C) by the direct temperature gradient technique under the pressure of inert gas pumped into an autoclave to avoid the solvent boiling. The main features of the solubility and growth kinetics are presented.

Twinning laws and twin types were studied for gallium phosphate grown by modified hydrothermal method. The twins were found to be formed in accordance with Brazil, Douphine and Leydolt's laws; such twins are characteristic for 32 class symmetry.

Brazil twins are typical for GaPO<sub>4</sub> single crystals. Douphine and Leydolt's twins occur very rear. The main specific feature of Brazil twins is an appearance of two planes of twinning right and left individuals; one plane  $\pi(10.2)$ , similar to quartz, berlinite and GaPO<sub>4</sub> crystals grown hydrothermally at T<300°C. The second plane is the other rhombohedron  $\pi'(01.2)$ . Earlier such twinning was not found in crystals grown at low temperature.

The quantity of twins depends very much on crystallographic orientation of initial seeds. To eliminate the twin quantity, the specific orientation, shape and size of seeds were found on the base of crystallographic and kinetic data for gallium phosphate single crystal growth.

**PS16.03.10 SINGLE CRYSTAL GROWTH OF Sr<sub>2</sub>RuO<sub>4</sub> BY LASER-HEATED PEDESTAL GROWTH (LHPG).** Y. P. Mascarenhas, D. Reyes Ardila, M. R. B. Andreetta, S. L. Cuffini, A. C. Hernandez, J. P. Andreetta, Instituto de Física de São Carlos, Universidade de São Paulo, C. P. 369, 13560-970, Sao Carlos, SP, Brazil

Sr<sub>2</sub>RuO<sub>4</sub> was reported in 1994 (1) as the first non-cuprate layered perovskite that is superconducting near 1K. Although its T<sub>c</sub> is so low, this layered oxide compound is the first directly relevant superconductor, without copper, for comparison with the high-T<sub>c</sub> cuprates. Besides, this results demonstrated that the presence of copper is not a prerequisite for the existence of superconductivity in layered perovskite compounds. Up to now, the method used in the preparation of single crystal was floating zone melting (2). We report, for the first time to our knowledge, the growth of Sr<sub>2</sub>RuO<sub>4</sub> single crystal fibers by Laser-Heated Pedestal Growth (LHPG) technique. The fibers obtained were up to 20mm in length with 0.8-1.0 mm in diameter. They were easily cleaved, yielding plate-like crystal with (001) surface. Sr<sub>2</sub>RuO<sub>4</sub> compound has K<sub>2</sub>NiO<sub>4</sub> structure with space group I4/mmm and lattice parameters a = 3.861 (1) Å and c = 12.701 (3) Å, which are in good agreement with the previous reports (3). The single crystal fibers were characterized by SEM, EPMA and X-ray diffraction using Laue method and single crystal diffractometer (CAD-4 Enraf-Nonius).

(1) Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz and F. Lichtenberg, *Nature* Vol. 372, p. 532 Dec. (1994).

(2) F. Lichtenberg, A. Catana, J. Mannhart and D. G. Schlom, *Appl. Phys. Lett.* 60, 1138-1140 (1992).

(3) L. Walz, F. Lichtenberg, *Acta. Cryst.* C49, 1268-1270 (1993).

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