

**P16.03.26***Acta Cryst.* (2008). A64, C588**Glycothermal growth of yttrium aluminium garnet nanocrystals**

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The glycothermal reaction of a stoichiometric mixture of aluminium isopropoxide and yttrium acetate in 1,4-butanediol (1,4-BG) at 300 °C directly yielded crystalline yttrium aluminium garnet (YAG) with the crystallite size of 28 nm. The crystallization of YAG in 1,4-BG takes place as follows: An intermediate, HO(CH<sub>2</sub>)<sub>4</sub>-O-Al<, is formed by the alkoxyl exchange reaction between aluminium isopropoxide and glycol. The cleavage of the C-O bond in HO(CH<sub>2</sub>)<sub>4</sub>-O-Al< yielding protonated tetrahydrofuran and aluminate ion is facilitated by participation of the intramolecular hydroxyl group. Ease in the cleavage of the C-O bond seems to be the prime factor for the formation of crystalline YAG. On the other hand, the gelatinous product was formed in glycothermal reaction in ethylene glycol because C-O bond of ethylene glycol is more difficult to be cleft than that of 1,4-BG. Rietveld analysis of YAG synthesized by glycothermal reaction in 1,4-BG indicated the presence of Al vacancies in the 24d sites and oxygen vacancies in the 96h sites, and partial substitution of Al ions in the 16a sites with Y ions was also suggested. Rapid crystal growth in the glycothermal reaction and the absence of mechanisms for elimination of defects, such as the dissolution-crystallization mechanism operated in hydrothermal reactions, are the reasons for the formation of defects. Al vacancies in the 24d sites and oxygen vacancies disappeared for YAG calcined at 1000 °C but the ratio of substitution of Al ions in the 16a sites with Y ions increased as compared with as-synthesized YAG. Although the solid solution of YAG did not appear in the stable phase diagram, YAG with Y-rich composition could be synthesized by glycothermal reaction.

Keywords: crystal growth, nanocrystals, defect structures

**P16.03.27***Acta Cryst.* (2008). A64, C588**Peculiarities of the growth of KDP crystals in non-stoichiometric solutions**Dmitry A Vorontsov<sup>1</sup>, Vadim N Portnov<sup>1</sup>, Vladimir P Ershov<sup>2</sup><sup>1</sup>University of Nizhny Novgorod, Department of Physics, Gagarina Ave., 23, building 3, Nizhny Novgorod, Nizhegorodskaya oblast, 603950, Russia,<sup>2</sup>Institute of Applied Physics, Nizhny Novgorod, Russia, E-mail: vorontsova@mail.ru

The stoichiometric composition of solution has a significance influence on the optical homogeneity and laser strength of KH<sub>2</sub>PO<sub>4</sub> (KDP) crystals. Existing theoretical models (A.A. Chernov, A.V. Nardov and C.V. Moshkin) predicts the maximum of growth rate for binary crystal in solutions with stoichiometric composition. There is an actual problem about the growth units by which mass transfer between the crystal and solution occurs. It was ascertained that the growth rate of {100} faces of KDP crystal goes through the minimum in stoichiometric solution at a constant supersaturation and temperature. This behavior is not described by known theoretical models. Thus, investigation the growth of KDP crystals from non-stoichiometric solutions in detail represents a challenge. In this research, the growth kinetics of the {100} faces of KDP crystals has

been studied in non-stoichiometric solutions with H<sub>3</sub>PO<sub>4</sub> and KOH additives. The normal growth rate has been measured by the precision laser polarization interference technique. It has been shown that the growth rate represents minimum in stoichiometry and increases with deviation of a solution from the stoichiometric composition at a fixed temperature and supersaturation. We calculated concentrations for different types of particles (ions and molecules) in KDP solutions at a given stoichiometry. The increase of the growth rate has been compared with the change of the particle concentrations versus solution stoichiometry. It has been made an assumption that K<sup>+</sup> and H<sub>3</sub>PO<sub>4</sub> in H<sub>3</sub>PO<sub>4</sub> doped solutions and K<sup>+</sup> and HPO<sub>4</sub><sup>2-</sup> ions in solutions with KOH are responsible for the mass transfer between the growing KDP crystal and bulk solution.

Keywords: crystal growth from solution, kinetics and mechanism of crystal growth, nonlinear optical materials

**P16.03.28***Acta Cryst.* (2008). A64, C588**Solvothermal synthesis of rare earth-iron mixed oxide**

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Solvothermal reaction of ytterbium acetate with iron acetylacetonate (Fe(acac)<sub>3</sub>) in 1,4-butanediol in the presence or absence of 1,6-hexanediamine at 300 °C for 2 h directly yielded hexagonal-YbFeO<sub>3</sub> (*P6<sub>3</sub>cm*). The product had a crystallite size of 32 nm and was composed of hexagonal plates with 20 – 30 nm width. The reaction of acetates of rare earth elements other than ytterbium also gave hexagonal-REFeO<sub>3</sub> (Ho – Yb). On the other hand, orthorhombic-YbFeO<sub>3</sub> (*Pbnm* with perovskite structure) was synthesized by the reaction of ytterbium chloride with Fe(acac)<sub>3</sub> in 1,4-butanediol in the presence of 1,6-hexanediamine. The product was comprised of irregularly-shaped particles with 80 – 100 nm size, and this particle size was essentially identical with the crystallite size (76 nm). Orthorhombic-REFeO<sub>3</sub> was also obtained by the reaction of chlorides of Dy – Yb in the presence of 1,6-hexanediamine; However, mixtures of RE(OH)<sub>2</sub>Cl, Fe<sub>2</sub>O<sub>3</sub>, RE<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> or REFeO<sub>3</sub> were obtained by the reaction of chlorides of rare earth elements with larger ionic sizes. Effect of the structure of amines on the solvothermal reactions of ytterbium chloride with Fe(acac)<sub>3</sub> was examined. Phase-pure orthorhombic-YbFeO<sub>3</sub> was obtained by the reaction in the presence of 1,6-hexanediamine or 1,8-octanediamine; however, the reaction in the presence of the other amines resulted in formation of unknown phase and/or Fe<sub>2</sub>O<sub>3</sub> together with orthorhombic-YbFeO<sub>3</sub>.

Keywords: perovskite oxides, nanocrystals, crystallization method

**P16.04.29***Acta Cryst.* (2008). A64, C588–589**Langbeinite-type phosphates K<sub>2</sub>Ln<sub>1.5-x</sub>Nb<sub>0.5+x</sub>(PO<sub>4</sub>)<sub>3</sub> (Ln = Sc, Y, In, Ho-Lu): Synthesis and structure**Artem A. Babaryk<sup>1</sup>, Igor V. Zatovsky<sup>1</sup>, Vyacheslav N. Baumer<sup>2</sup>, Nikolay S. Slobodyanik<sup>1</sup>, Oleg V. Shishkin<sup>2</sup><sup>1</sup>Kyiv National Taras Shevchenko University, Chemistry Department, Volodymyrska str. 64, Kyiv, none, 01033, Ukraine, <sup>2</sup>National Academy of Science of Ukraine, Lenina ave. 60, Kharkiv, 61001, Ukraine, E-mail :

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Langbeinite-type ( $\alpha$ - $K_2Mg_2(SO_4)_3$ [1]) phosphates has been intensively investigated over the last decade. In particular, to continue the search of the relationship with large family of  $\{[M_2(PO_4)_3]^{n-}\}$ ; anionic framework, which covers NASICON (Na Supersonic Conductor),  $ScWO_4$ , Garnet structure types, is being of great interest. In this work the new synthetic approach is applied for single crystal obtaining, following structure investigation of Langbeinite-type phosphates  $K_2Ln_{1.5-x}Nb_{0.5+x}(PO_4)_3$ , where  $Ln = Sc, Y, In, Ho-Lu$  is subject of this report. The corresponding compounds were grown in spontaneous crystallization mode from fluxes of melted systems  $KPO_3$ - $K_4P_2O_7$ - $LnF_3$ - $K_2NbF_7$ . All synthesized tetragonal-shaped crystals belong to the cubic system (sp. gr.  $P213$ ). Single crystal structure determination revealed correlation between the composition of target compounds and radii of trivalent metal cations. Analysis of potassium, lanthanide and phosphorus bonding parameters (BVS method) allows consider crucial role of phosphate tetrahedron on total stability of the structure.

[1] Zemann, A., Zemann, J. (1957) *Acta Cryst.*, **10**, 409-413.

Keywords: phosphates, X-ray crystal structure analysis, crystal synthesis

### P16.04.30

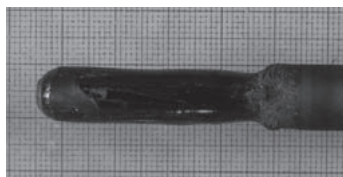
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#### Growth of large single crystals of high-Tc superconductor using a tilted-Lamp floating zone furnace

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The intimate connection between superconductivity and magnetism in high-Tc cuprates is believed to be fundamental to the superconducting mechanism. So, extensive neutron-scattering measurements had been carried out on  $La_{2-x}Sr_xCuO_4$ . Since  $La_{2-x}Sr_xCuO_4$  has small neutron scattering cross-section, large volume of single crystals were needed for these measurements. Typical single crystals grown by Traveling Solvent floating zone method are 5 mm in diameter and few centimeters in length. To accommodate large volume of single crystal in the neutron beam several single crystals are aligned in the beam. This process also leaves empty spaces in between and hence unused part of neutron beam. To overcome these problems here we have grown  $La_2CuO_4$  single crystal of diameter about 10mm, almost twice of that grown until now (Fig. 1). A specially modified floating zone furnace, Tilted-Lamp Floating zone furnace, where the ellipsoidal mirrors could be tilted downward up to 30 degrees was used for this experiment. Optimum tilting of the mirror-lamp systems modifies the heating profile of the molten zone in a way that we believe, is favorable for growth of single crystals with larger diameters.



Keywords: tilted-lamp floating zone, single crystal  $La_{214}$ , high-Tc Superconductor

### P16.04.31

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#### Solid-liquid interface in floating zone growth of rutile crystal with variation of focusing angle

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In the floating zone (FZ) method, the molten zone is kept between a feed and a grown crystal by the balance in gravity and surface tension of the melt. Therefore, stable molten zone is necessary for good crystal growth. In infrared convergence type FZ, the molten zone is heated from the surface. So the shape of the solid-liquid interface is usually convex for many materials, which often makes it difficult to grow large crystals in diameter, because the interface becomes more convex as the diameter increases. In our experiment, we focused on the locations of heating lamps and the molten zone. In conventional heating system, the locations are in the same horizontal plane. In our experiment, these locations were systematically changed. Heating lamps and reflecting mirrors were tilted from the horizontal configuration to 20 degree by 5 degree as step for the crystal growth of rutile ( $TiO_2$ ). To examine the interface shapes, molten zones were quenched. However, the shapes of solid-liquid interfaces were not clear by polarized optical microscopy. To evaluate the shapes by chemical analysis of EPMA, Yttrium was added in the molten zone because Yttrium is very hard to dissolve in the grown crystal of rutile. By using this technique, we could successfully investigate the interface shapes precisely. Focusing angle dependence of the interface shapes would be reported.

Keywords: float zone growth, oxides, interface characterization

### P16.04.32

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#### Growth of Nd-doped $YVO_4$ single crystals by anisotropic heating floating zone method

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Nd-doped  $YVO_4$  single crystals was grown along the a-axis by anisotropic heating floating zone (AHFZ) method.  $YVO_4$  single crystals has strong tendency to grow along the c-axis. For normal floating zone (FZ) method, the grown crystals show a flat shape, longer in the c-axis. The average aspect ratio shows 1.4 (c-axis diameter / a-axis diameter) in normal FZ method. To make the shape of crystals round type, AHFZ method was tried. The powder of  $Y_2O_3$ ,  $V_2O_5$  and  $Nd_2O_3$  was mixed with  $V_2O_5$  richer than the stoichiometric composition. Nd of 3at% was substituted for Y sites in  $YVO_4$ . The mixture was calcined at 600°C for 15 hrs, and sintered at 1500°C for 6 hrs. In case of AHFZ machine, the electric power of two pairs of lamps (A and B lamp pairs) located at the diagonal positions can be controlled independently. The c-axis of seed crystal was positioned along B lamp pair direction. The a-axis of seed crystal was positioned along A lamp pair direction. The voltage ratio [c-axis voltage / a-axis voltage] (=B lamp pair voltage / A lamp pair voltage) was changed from 0.7 to 1.3. As the voltage ratio was changed from 0.7 to 1.3, the aspect ratio of crystal (c-axis diameter / a-axis diameter) changed from 1.05 to 1.88. In case the electric power applied to c-axis of crystal is stronger than the electric power applied to a-axis of crystal,