

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

Saburo Hosokawa, Yusuke Tanaka, Hyung-Joon Jeon, Shinji Iwamoto, Masashi Inoue

Graduate School of Engineering, Kyoto University, Department of Energy and Hydrocarbon Chemistry, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan, E-mail: hosokawa@t04.mbox.media.kyoto-u.ac.jp

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: vorontsovda@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**

Hyung-Joon Jeon, Saburo Hosokawa, Shinji Iwamoto, Masashi Inoue

Graduate School of Engineering, Kyoto University, Department of Energy and Hydrocarbon Chemistry, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan, E-mail: JEON.H@hy2.ecs.kyoto-u.ac.jp

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 :