babaryk@bigmir.net

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), ScWO₄, 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 KPO₃-K₄P₂O₇-LnF₃-K₂NbF₇. 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

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

A.T.M. Nazmul Islam^{1,2}, I. Tanaka², S. Watauchi²

¹Hahn-Meitner-Institut, SFN1, 100 Gleinicker strasse, Berlin, Brandenburg, 14109, Germany, ²Center for Crystal Science and Technology, University of Yamanashi, Miyamae 7-32, Kofu, Yamanashi 400-8511, Japan, E-mail:nazmul.islam@hmi.de

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 La2-xSrxCuO4. Since La2-_xSrxCuO₄ 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 La₂CuO₄ 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 La214, high-Tc Superconductor

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

<u>Md. Abdur Razzaque Sarker</u>, Watauchi Satoshi, Tanaka Isao University of Yamanashi, Center for Crystal Science and Technology, Miymae 7, Kofu, Yamanashi, 400-8511, Japan, E-mail : g08df004@ yamanashi.ac.jp

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 (TiO₂). 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

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Growth of Nd-doped YVO₄ single crystals by anisotropic heating floating zone method

Dal Hoy Kwon, Satoshi Watauchi, Isao Tanaka

University of Yamanashi, Center for Science and Technology, Faculty of Engineering, Miyamae 7, Kofu, Yamanashi, 400-8511, Japan, E-mail : kwondalhoy@hotmail.com

Nd-doped YVO₄ single crystals was grown along the a-axis by anisotropic heating floating zone (AHFZ) method. YVO₄ 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 Y₂O₃, V₂O₅ and Nd₂O₃ was mixed with V₂O₅ richer than the stoichiometric composition. Nd of 3at% was substituted for Y sites in YVO₄. 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, the crystal diameter increases into c-axis direction. In contrast, when the electric power applied to the a-axis of crystal is stronger than the electric power applied to c- axis of crystal, the crystal diameter increases into the a-axis direction. As a conclusion, to get the round shape crystal, the electric power of the lamp applied into a-axis direction of crystal should be stronger than c-axis direction of crystal.

Keywords: crystal growth, float zone growth, vanadium compounds

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Chiral and achiral mechanisms of regulation of calcite crystallization

<u>Mihoko Maruyama</u>¹, Katsuo Tsukamoto¹, Gen Sazaki^{2,3,4}, Yoshihiro Nishimura^{1,6}, Peter G Vekilov⁵

¹Graduate School of Science, Tohoku University, The Earth and Planetary Materials Science, 6-3, Aoba, Aramaki, Aoba, Sendai, 980-8578, Japan, Sendai, Miyagi, 980-8578, Japan, ²Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan,, ³Center for Interdisciplinary Research, Tohoku University, Aramaki, Aobaku, Sendai 980-8578, Japan,, ⁴Department of Electrical Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan,, ⁵Department of Chemical and Biomolecular Engineering and Department of Chemistry, University of Houston, Houston, Texas, 77204, USA., ⁶Present address: Lasertec Corporation, 4-10-4 Tsunashimahigashi, Kohoku-ku, Yokohama, 223-8551 Japan,, E-mail:marumiho@ganko.tohoku.ac.jp

The regulation of calcite mineralization by chiral biological molecules is one of the fundamental unresolved issues at the interface between biological, geological, and physical sciences. Here we address the role of chirality of L-aspartic acid (L-Asp), a model additive, in the regulation of the calcite growth. We apply phase-shift interferometry to non-intrusively monitor in situ the morphology of the surface and quantify the velocity of propagation of the steps, during crystallization. Similar to complex behavior observed before, L-Asp leads to several-fold increase in the step velocity, in all directions, at low supersaturations, and several-fold slow down at high supersaturations. L-Asp also introduces asymmetry in the velocity of steps of related by mirror symmetry, however, of less than 10 %. To explain the complex effects of L-Asp, and, likely, of other biological regulators of calcite crystallization, we show that prior to incorporation into steps, calcium and carbonate ions adsorb on the terraces and diffuse towards the steps. L-Asp accelerates the surface diffusion towards the steps, an achiral process, likely due to rearrangement by L-Asp of the structure of the water coating the calcite crystal surface. Importantly, L-Asp delays by about 20 times the incorporation of calcite ions into the steps, the only chiral process in the calcite crystallization mechanism, likely by blocking a significant fraction of the kinks. We show that the low asymmetry between the two chiral directions due to attenuation by the surface supply fields of the steps. The results and analyses presented here suggest that the chiral effects of bio-generated molecules on crystallization may be too weak to judge about biological or non-biological origin of minerals

Keywords: chirality, calcite, in-situ observation

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Formation of barred olivine texture 4.6 billion years ago

<u>Hitoshi Miura</u>¹, Yokoyama Etsuro², Tsukamoto Katsuo¹, Nagashima Ken³

¹Tohoku University, Department of Earth Sciences, Aoba 6-3, Aramaki, Aoba-ku, Sendai, Miyagi, 980-8578, Japan, ²Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan, ³Osaka University, 1-1 Yamadaoka, Suita, Osaka 565-0871, Japan, E-mail : miurah@ganko. tohoku.ac.jp

Most of chondritic meteorites falling onto the Earth contain mmsized crystalline silicate spheres (chondrules), which are believed to have been formed from molten silicate droplets 4.6 billion years ago in our early solar system. Some of them have interesting textures with rim and bars. The rim has a thin shell-like morphology surrounding a chondrule. The bars are planar crystals parallel each other observed inside the rim. The remarkable features are that the rim connects with bars and the crystal orientation of the rim is the same as adjoining bars. Such texture has not been reproduced in the laboratory experiments except a few examples, therefore, the formation mechanism is unclear. We notice that the Mullins-Sekerka instability at the interface between the previously formed rim and the inside melt results into the formation of bars based on the linear stability analysis of Mullins and Sekerka (1964, J. Appl. Phys. 35, 444). We numerically simulate the crystallization of a supercooled silicate droplet by using a phase-field model. For simplicity, we consider a droplet of one component in our model, so we solve the equations for evolution of phase and temperature fields, but do not the equation of concentration. Initially, we assume that the rim is formed at the droplet surface. Since the rim is heated up to about the melting temperature by the release of the latent heat of crystallization, the temperature gradient from the hotter rim to the cooler inside is generated. In this situation, the interface between the rim and the inside melt is unstable during the solidification. Our simulation shows that the instability grows nonlinearly and parallel planar crystals are formed. This morphology is very similar to that observed in some natural samples of chondrules.

Keywords: crystal growth of silicates, supercooling, instability

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Property and morphology of organic modified CeO₂ nanocrystals synthesized in supercritical water

<u>Tadafumi Adschiri</u>¹, Jing Zhang¹, Seiichi Takami¹, Takashi Naka², Masahiko Ito¹, Yoshiyuki Kawazoe¹

¹Tohoku University, Advanced Institute for Materials Research(WPI-AIMR), 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan, ²Tsukuba University, 1-1-1, tennoudai, tsukuba-shi, Ibaraki, 305-8571, Japan, E-mail:ajiri@tagen.tohoku.ac.jp

We proposed a new method to synthesize organic-inorganic hybrid nanoparticles at supercritical hydrothermal conditions. By introducing organic legands (aminoacids, carboxylic acids, amines, alcohols, aldehydes etc.) into supercritical hydrothermal synthesis atmosphere, organic -inorganic hybrid nanocrystals are synthesized. For the case of CeO₂ nanocrystals, nanocubes with 100 surface could be synthesized. It is the first report that CeO₂ nanocrystals with 100 surface that has extremely high catalytic reactivity can be synthesized. With increasing the amount of surface modifier, shape of the nanocrystals was changed to trancated octahedron with 100