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Keywords: lanthanide orthovanadate, bulk spiral growth, Hartman-Perdok (HP) theory

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Mechanism of formation of $Na_xV_2O_5$ bronze crystals grown from the melt by czochralski method

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Recently a new technique of manufacturing of nanoelectrical and nanomechanical devices has been offered. The method is formation of nanostructures on substrates by thermo-electrical operation of atoms or atoms complex currents in the direction probe-substrate or substrate-probe in automatic regime [1, 2]. Practical realization of such nanostructure formation technique demands to create bulk-active probes with emission-getter functions and to use scanning tunnel microscope of special construction to control the adsorption-desorption processes. The structural peculiarities of oxide vanadium bronze allow to emit interstitial atoms from channels of V-O skeleton on a substrate or, on the contrary, to remove atoms from a substrate and introduce them into the structural channels of the needle- probe. Increasing of cations content in homogeneous region does not influence on V-O skeleton, but physical-chemical properties vary non-monotonously.

The present paper demonstrates the structural-morphological peculiarities of β-$Na_{0.28}V_2O_5$ crystals growing from the melt in air and in reducing atmosphere by Czochralski method. Optical microscopy and STM images of surface relief for as-grown planes and cleavage planes as well as photometric analysis of REM images of lateral surface and spectra of reflex brightness in visible before and after vacuum annealing are given. Scanning tunnel microscopy was also used for observation of absorbtion-desorbtion processes on substrate with the help of emission-active probe ($Na_{0.33}V_2O_5$) in tunnel regime.

It was shown that the difficulties are arising mainly from polycrystallization during growth and breakage after crystal growth. For Cz-bronze a dendritic shape is generated during the crystallization process. Surface morphology is formed of cleavage faces of the crystal. We could observe sets of nearly parallel steps on {100} planes prolonged along growth "b" axis. Thick steps were composed of two to twenty terraces. They have "V-shaped" structures which always tend to become rounded. Terraces were usually around 240nm in height. Lateral planes of such terraces were disoriented of ≈15° relatively to each other. The height of each thick step was around 1.2 μm. The terraces were usually originated from the seed. Such growth mechanism has an important role in the formation of structure imperfections. The bulk consists of two-dimensional layers in a highly crystalline and oriented form which prolong along growth direction. It revealed that oxygen was doped into the bronze ingot while it was grown in air atmosphere. Investigations of as-grown bronze $Na_xV_2O_5$ behavior at thermal treatment in vacuum also estimated the definite role of oxygen in structure formation of Cz-$Na_xV_2O_5$ bronze. X-ray phase analysis of as-grown Cz-bronze and X-ray structure analysis in temperature interval 25-320 °C were carried out to confirm phase homogeneity and thermal stability of Cz-$Na_{0.28}V_2O_5$ crystal.

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Keywords: oxide_vanadium_bronze, Czochralskii_growth, morphology

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High Quality Protein Crystal Growth under Microgravity in JAXA PCG project

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Japan Aerospace Exploration Agency High Quality Protein Crystal Growth project (JAXA PCG) had six flight opportunities from 2009 to 2012, followed by the previous JAXA-GCF, JAXA-New-GCF project. We produced various know-how of protein crystallization experiment in space in these projects.

The protein samples are transported by Russian Progress Spacecraft to the ISS in cooperation with Federal Space Agency of Russia (FSA) and are placed in the Protein Crystallization Research Facility (PCRF) in Japanese Experiment Module "Kibo" (JEM) for 2-4 months.

The experimental opportunities are provided for Japanese national project targeting the biological protein molecules to clarify diseases and life phenomenon, for JAXA strategic mission to get results through the space experiment, for technical development to crystallize membrane protein and protein-ligand complex and for international cooperation for Russian user and Asian nations such as Malaysia.

We used "Gel-Tube method", a kind of counter-diffusion method, for crystallization. In the counter-diffusion method PEG and salt are diffused into the protein solution in a capillary and increased their concentrations gradually up to those in the precipitant solution. We introduce some experiments to know optimum salt concentration for crystallization which will be helpful for reconsideration of the salt concentration in the PEG solution if crystallization fails even by the vapor-diffusion method.

We developed the method by which we estimated the effectiveness of crystallization under microgravity environment and optimized the crystallization condition in space.

We treated more than 100 proteins onboard "Kibo". In this presentation the latest scientific results related to positive effect of microgravity environment for creating high quality crystals are introduced. Some crystals obtained in International Space Station showed the high resolution data to contribute greatly to designing new drug or new functional catalyst.

Key words: microgravity crystallization, international space station, high-resolution protein structures

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Pure $NaNO_3$ crystal growth

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Our purpose is to study the crystal growth kinetics of sodium and potassium nitrates and the morphology change due to the presence of foreign atoms into the crystallizing solution. Moreover, we also investigate the different growth rate as a function of those 'impurity' atoms. We also study the theoretical equilibrium morphology and the possible epitaxy between nitrates that can conduct to a change in morphology.

As a first step of the work we designed and built a special device to study growth kinetics either in pure systems or with impurities addition mainly of other nitrates.

The unit consists in four main bodies: an observing cell, a peristaltic pump, 2 thermostat baths with heat exchangers and a reservoir. The solution (of known concentration) leaves the reservoir at a temperature somewhat higher than the target temperature with the aim of the pump. It goes through a heat exchanger directly to the observing cell, where a crystal is glued and can be observed in a microscope. Immediately after leaving the cell its temperature is raised again with another heat exchanger that conducts to the reservoir. A 1 liter reservoir of solution is enough to have a constant concentration throughout all experiment. True growth temperature can be recorded continuously; there are two sensors into the solution at less than 5mm from the crystal.

With this unit we are able to control the main parameters that have an influence in the crystal growth which are: flow rate and growth temperature i.e. the supersaturation ratio.

It was found that $NaNO_3$ is very temperature sensitive. The metastable region is quite narrow, for a given concentration the gap between crystallization and dissolution can be less than 1ºC [1]. Therefore we have to work in a very accurate way in order to control its behavior. Thus, all precaution cited above are self-explained to monitor experiments.

As in the literature found there is not an agreement in the $NaNO_3$ solubility curve we first re-determined it by the method proposed by Beckmann, W., Boistelle, R., and Sato, K. [2]. It consists in observing a crystal looking for a temperature in which it neither dissolves nor growths. This allows us to work at known supersaturation in the following experiments.

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The effect of foreign particles on the interface shape during solidification of crystals

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The shape of a solidifying interface is generally affected when it encounters foreign inert particles. The degree of deformation depends on the morphology and physical properties of the particles [1-4]. The overall effect also affects the pushing and captures process, when pushing is present.

In the present report the interaction between particle and interface is analyzed by means of a mathematical model employing the finite element method. The effect on the interface of different particle shapes and relative thermal conductivities between particle and melt was studied.

The results sown that for an isolating particle with respect to the melt the interface is convex in a degree that changes depending on the particle shape and separation distance from the interface. The particle geometries considered for simplicity were spherical, cylindrical, conical and semi-spherical. For a conducting particle the interface changes to concave.

From the observation of the present results the trapping of the particles by the solid starts in different places; for a conducting particle the first points touching the solids are the corners while for an isolating particle this occurs at the particles center.

The analyses of these observations indicate that the probability of pore formation could be higher when isolating particle are present in the melt.

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Nucleation of gypsum at low supersaturations

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Crystallization from solution in natural environments mostly occurs at low to very low supersaturation. An example of this are the giant gypsum crystals of Naica (Mexico), where nucleation occurred at supersaturations very close to solution equilibrium [1]**.** Although nucleation is a well studied process in the laboratory, the majority of investigations focus on a high to medium supersaturation range. To attain a meaningful extrapolation from kinetic data obtained in the laboratory to natural conditions information on nucleation kinetics from low to very low supersaturated solutions are necessary. Therefore in this work, a method for studying the nucleation process at low supersaturations is proposed and this approach is applied to the case of crystallization of giant gypsum crystals at Naica.

Nucleation of gypsum was studied within low supersaturation ranges at 20 and 55 ºC. Experiments were carried out in 0,2 ml batch reactors with no stirring, using a temperature controlled chamber at 20 ºC, and a peltier based thermostatic multi-well set up, coupled to an inverted microscope (Nikon Eclipse TE2000-S) for the experiments at 55 ºC [2]. All experiments were covered by a layer of mineral oil and sealed hermetically in order to avoid evaporation. The induction period (the time necessary for nucleation to take place) was measured by single microscope observation in all experiments.

As predicted by classical nucleation theory, an inverse relation in the induction period with temperature and supersaturation was found. Estimating the value of interfacial tension from the experimental data, we have compared the calculated values with values reported in literature obtained for homogeneous nucleation experiments [3,4,5]. Applying the kinetic model proposed by Liu [6,7] we found that gypsum has a very large susceptibility for heterogeneous nucleation (which also corresponds with our observations), and values of interfacial tension found in literature should be higher than reported. From these data we were able to extrapolate induction times for very low supersaturations (similar to those found in the waters of Naica, Mexico [1]). Thus, studying nucleation kinetics at low supersaturations allows us to access information on geological time scale crystallization processes occurring in Nature through laboratory experiments.