CRYSTAL GROWTH BY PRECIPITATION UNDER MICROGRAVITY*

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ABSTRACT

After having stressed the importance of understanding the mechanisms associated with defect generation during growth and the influence of gravity, the experiment planned for FSLP is described. The advantages of adapting this experiment to the FES are then discussed. A brief survey of the ground based research under way is given.

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INTRODUCTION

The influence of growth defects on many physical properties is well known. Semiconductors, piezoelectrical, electrooptical, LASER crystals are good examples. It is therefore very important to learn how defects arise, how to control them and thus how to produce higher quality crystals. These crystals are grown by various methods, from the melt, from the solution or from the vapour phase. The nature of the defects produced during growth depends in general much more on which one of these growth techniques is being used and how far from thermal equilibrium growth is performed than on the actual chemical nature of the crystal. This is particularly true in the case we shall be dealing with in this paper, namely growth from the solution. It is therefore better to perform these studies on model crystals which are easiest and fastest to grow and are best fitted for the study of defects and the derivation of general laws on the generation of defects. It will of course be still better if these crystals have interesting physical properties which could be tested in crystals with different crystalline perfection and on crystals grown on earth and under microgravity conditions.

The major growth defects are growth bands and growth striations, growth sector boundaries, inclusions and dislocations (1),(2). Growth bands are many in nature, ranging from very thin defects nearly one atomic layer in thickness to layers in inclusions and to periodic variations of the lattice parameter associated to corresponding variations in impurity content or vacancy concentration. The origin of these defects is usually attributed among other causes to convectional instabilities associated to temperature gradients or to temperature fluctuations. The main factor for these convection effects is gravity which correlates temperature differences and mass transfers. The various parameters which govern the growth processes and on which the origin of growth defects depends are supersaturation, temperature, pressure, nature and velocity of the solution flux etc ... These parameters are not independent, in particular precisely because of the presence of gravity. In order to understand the influence of these various parameters on the generation of defects it is necessary to be able to vary them independently. A good way to do that is to perform the growth under microgravity conditions so that convection effects should be considerably reduced.

PREVIOUS STUDIES ON THE RELATIONS BETWEEN GROWTH DEFECTS AND GROWTH CONDITIONS

Many studies have been performed in our laboratory on the characterization of growth defects and on the relations between growth conditions and growth defects. These experiments have been carried out on calcite (3), (4)(5), KDP and KDKP (6,(7), TGS (8), germanates (9), potash alum (10)(11). The various types of growth defects which may arise were identified. In many cases the relation between the growth rate of a face and the screw character of dislocations intersecting this face was clearly demonstrated. Different types of growth defects appear when a perturbation is voluntarily introduced at a given type during growth. Depending on the intensity of the perturbation it may be a very thin growth band or a growth band decorated with inclusions generating or not dislocation bundles. The influence of the solution flux on the generation of defects was established. In particular, it was shown that dislocations are formed on the side of the crystal facing the flux and that liquid inclusions are trapped at the backside which stop dislocation propagation. The development of these defects depends on the values of the supersaturation and of the flux rate and the influence of these parameters was systematically studied. The best quality crystals are obtained when the crystal is stationary with respect to the solution.

DESIGN OF THE EXPERIMENT TO BE PERFORMED IN FSLP

In order to increase crystalline perfection convections should be avoided and growth performed in a purely diffusional system. It can be shown that growth rates would be extremely long in that case (12) unless a concentration gradient is imposed in some way. One way is to create a temperature gradient between the crystal seed and the solution as proposed by R. LAL (13) for the FES. This may however be the sources of inner stresses within the growing crystal. Another way is that used by D. LIND(14) for the growth of crystals by coprecipitation from the solution in ASTP. We had already used this technique for the study of the habit of calcite crystals depending on the nature of impurities (15).

The principle of the experiment is as follows. Two solutions AB and CD are contained in two compartments 1 and 2 separated by a third one containing a neutral solution N. At the beginning of the experiment compartments 1 and 2 are put in communication with the third one and the solutions AB and CD are allowed to diffuse in it. When they meet, a reaction takes place of the type :

$$AB + CD \rightarrow \underset{\downarrow}{AC} + BD$$

BD remains in the solution and AC which is very little soluble precipitates.

D. LIND'S set up in the following :

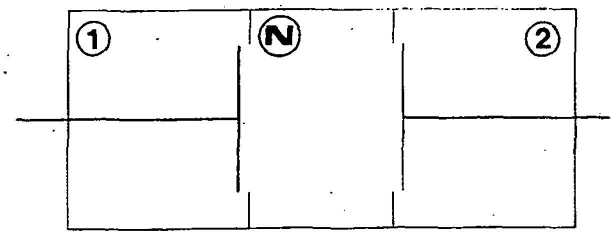

Figure 1

Two pistons are pulled back at the beginning of the experiments thus putting compartments 1 and N, and 2 and N in communication.

In the experiment which we shall perform in FSLP, we shall use a cell of a completely different design in a thermostat where the temperature will be constant to $\pm$ 0.1° C. In our design, compartments 1 , 2 and N are concentric cylinders, 1 and 2 being annular and on the outside and N an inner cylinder :

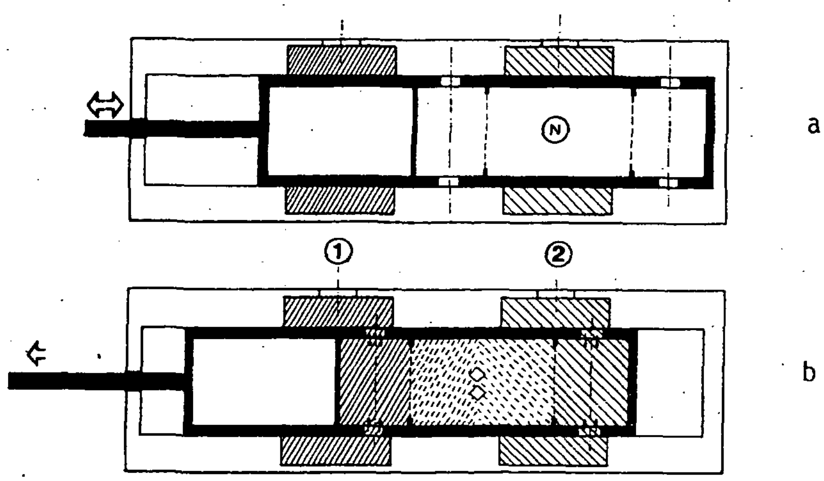

Figure 2

There are openings on the lateral side of the inner cylinder. Before the experiment starts, they do not lie in front of the outer compartments (fig. 2a). By translating the inner cylinder by means of a motor, the openings can be brought in front of compartments 1 and 2 (fig. 2b). Solutions AB and CD then diffuse in the inner compartment. Porous diaphragms on each side of the central reactive cell ensure that the solution flow is laminar. With thisset up the compartments are put in communication at constant volume. Furthermore, the movement of the cylinder during the opening will be extremely slow (it will take about half an hour). For all these reasons there will be minimum perturbation of the diffusion flow during the opening process and afterwards. The dimensions of the cell have been determined after calculating the diffusion profiles in order to optimize maximum growth during the time alloted for the experiment (about 90 hours).

The crystals to be grown in the experiment are various phosphates of divalent cations, in particular calcium and lead. They have been chosen on one hand because they grow fast (it is possible to obtain crystal platelets one centimeter accross in a few days) and in a shape which allows X-ray topographic studies of the as grown crystal without any cutting to be required, and on the other because they have interesting properties, either physical (lead phosphate is ferroelectric) or biological (calcium phosphate). In the future, other phosphates such as aluminum or lanthanum may also be considered because of their highly interesting physical properties. The type of chemical reaction which will be used will be, for instance in the case of brushite, of the type

$$NH_4\,H_2\,PO_4 + Ca(No_3)_2 \rightarrow \frac{Ca\,H\,PO_4,\ 2H_2O}{\downarrow}$$

GROUND BASED EXPERIMENTS

The present ground based research is carried out along two main directions. One is concerned with hydrodynamic studies and calculation of diffusion profiles. The other one is concerned with growth in purely diffusional conditions. A good way to achieve this result on earth is to use gel growth. We are using it for growing both brushite (16)(17) and lead phosphate. It has been checked that purely diffusional conditions have indeed been achieved in our experiments and that FICK's law applies to a very good accuracy, whatever the diameter of the tubes used for the gel growth or the diffusion lengths. Several types of gels have been tested, with different densities and pH and the crystalline perfection is assessed in each case by X-ray topography. High quality crystals $10 \times 10 \times 0.5 mm^3$ have thus been obtained.

Furthermore, ground tests on the cell to be flown in FSLP are under way.

PROPOSED EXPERIMENT IN THE F.E.S.

The experimental set up available in the FES would allow us to perform simultaneously two types of experiments. The first one would be devoted to a continuous observation during the whole length of the experiment of the following growth parameters by means of the holographic system : solution flow and isoconcentration curves to be compared afterwards to calculated ones according to the diffusion theory, nucleation, position, number, growth rate and habit changes of the crystals, isoconcentration gradients around each crystal etc ... On the other hand, it would be extremely interesting to study the influence of a perturbation of the growth conditions on the growth and the generation of defects. This has already been shown in our earlier experiments and in a study by F.Mussard and S. Goldsztaub (18) who have grown sodium chlorate crystals under an interferometric optical microscope. They correlated local perturbations of the concentration gradient observed optically to the generation of dislocation bundles observed afterwards by X-ray topography and to a corresponding dramatic increase of the growth velocity of the face intersected by these dislocations. We therefore propose that the second experiment which could be performed would be study of a perturbation of a single growth parameter. The temperature would be maintained constant and a perturbation in the flow of matter would be introduced at half the time alloted to the experiment by traversing the inner cylinder respective to the outer compartment in order to cut the communication between compartments 1 and 2 and the neutral compartment and then to open it again. By means of the holographic system the perturbation of the solution flow and isoconcentration curves could be measured. X-ray topography of the crystals performed afterwards in the laboratory would show whether defects were generated due to the perturbation and of what nature.

CONCLUSIONS

Microgravity provides unique conditions for the study of crystal growth and the understanding of the generation of growth defects as well as for the obtention of high perfection crystals. The facility available in FES is very well suited for these types of studies since the holographic system will enable a continuous observation of the growth conditions and any observed change can be correlated afterwards to the defects observed in the crystals by X-ray topography.

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