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Letter to the Editors

A new technique for growing crystals from the vapor

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Abstract

A new method for growing single crystals with sensitive control of supersaturation and minimal influence from foreign surfaces is described.

The main problem encountered in accurately studying the kinetics of crystal growth from the vapor is the control of supersaturation near the crystal. One of the most intensely studied vapor-grown crystals is ice, for which the methods typically employed are growth in a diffusion chamber [1–3] or a convection chamber [4], and on a substrate [5–8]. These all involve gradients of temperature and vapor pressure that complicate analysis. The mechanical support of the crystal introduces two additional problems: competition for vapor between neighboring crystals, and influence of the support on faces in contact with it. We report here a simple way of minimizing these problems for the growth of ice crystals. However, this technique could be applied to other crystals as well. It is particularly well suited for the measurement of growth at low supersaturations where the growth rate is slow.

The problem of thermal and compositional gradients in the vapor is practically eliminated by using a supercooled melt of the crystal material as the vapor source. This approach utilizes the fact that, as schematically indicated in Fig. 1, the vapor pressure of a solid drops more rapidly with decreasing temperature than that of its supercooled melt. Introducing different amounts of a solute into the melt at constant temperature makes accessible the range of supersaturations between zero and saturation with respect to the pure melt, which is the maximum possible with this technique. In practice, we change temperature at constant solute concentration to get a range of supersaturations without starting a new run. The technique allows growth or sublimation without imposed temperature gradients. For ice growth, we use LiCl as the solute because of its low eutectic point.

The problems of parasitic crystals and perturbation of the crystal by its support are greatly alleviated by initiating ice growth in pure water in a thin capillary extending into the growth chamber (Fig. 2). Nucleation is accomplished after insertion of the filled capillary into the chamber at a temperature below 0°C by dropping little bits of dry ice into the stainless steel tube. The expansion due to freezing pushes a droplet out onto the tip (Fig. 3a), which then freezes (nearly always) as a single crystal. During growth of that crystal from the vapor, the

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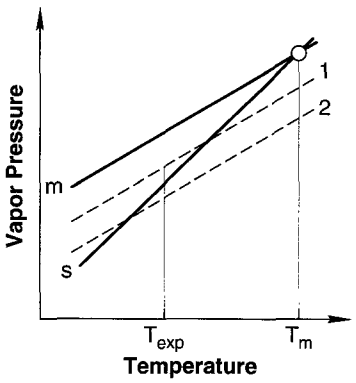

Fig. 1. Schematic vapor pressure curves of a melt (m) and its solid (s) below the melting point. Dashed curves indicate lowering of vapor pressure at two solute concentrations in the melt: (1) at the experiment temperature T_{exp}, the supersaturation is lower than that with pure melt; (2) a concentration that produces undersaturation at the same temperature.

capillary can influence at most one of the two basal and two of the six prism faces by direct contact. Temperature and vapor density gradients resulting

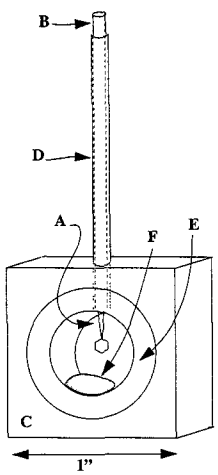

Fig. 2. The growth chamber. A crystal is grown at the tip of a fused silica capillary 2–10 μm in diameter (A) connected to a stainless steel tube (B) with outside diameter 6 mm via a brass plug and sealed with Apiezon black wax. The capillary projects into a 13 mm diameter hole in the brass block (C) through a brass tube (D) that is silver soldered to the block. Glass windows (E) are mounted on both sides of the hole with buna-n o-rings, sealing the growth chamber except for just enough gap between the brass and stainless steel tubes to allow rotation of the crystal. The growth chamber contains between 0.05 and 0.5 ml aqueous LiCl solution (F) that serves as the vapor source or sink. The growth chamber is enclosed in a stirred, constant-temperature bath.

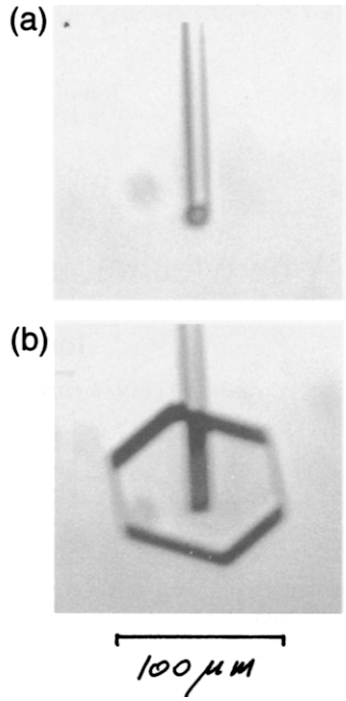

Fig. 3. Ice crystal grown in the chamber of Fig. 2. (A) Initial frozen droplet, −13.6°C. (B) The same crystal after 203 min growth below 1% supersaturation.

from the growth itself are minimized at low growth rates. Concentration changes during growth are negligible and the supersaturation remains constant as long as the solution has a much larger volume than the crystal.

The glass capillary tips were drawn down to the size shown in Fig. 3 by heating the middle of a 1 mm OD capillary hung from its top end, with a small weight attached to its bottom. Different capillary tapers can be produced by adjusting the size and temperature of the flame and the amount of weight. Extension of this technique to materials that contract upon crystallizing should be possible using short capillaries or by nucleating when there is already a small drop extruded from the tip.

Acknowledgements

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