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Flight Experiment to Study Double-Diffusive Instabilities in Silver-Doped Lead Bromide Crystals

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ABSTRACT

A detailed study on the effect of convection on crystal quality was carried out by growing lead bromide crystals in transparent Bridgman furnace. Direct observations were made on the solid-liquid interface and a new kind of instability was observed. This could be explained on the basis of toroidal flow in the AgBr-doped lead bromide sample. With the increasing translation velocity, the interface changed from flat to depressed, and then formed a cavity in the center of the growth tube. The crystal grown at the lowest thermal Rayleigh number showed the highest quality and crystal grown at the largest thermal Rayleigh number showed the worst quality. Numerical studies were carried out to provide a framework for interpreting the observed convective and morphological instabilities, and to determine the critical (limiting) concentration of dopant for a particular growth velocity and gravity level. Theoretical instability diagrams were compared with data obtained from the experimental studies. These studies provided basic data on convective behavior in doped lead bromide crystals grown by the commercially important Bridgman process.

1. OBJECTIVES:

The main objective of the present program is to understand thermosolutal convection during crystal growth of $PbBr_2$-AgBr alloys. This involves identification of the growth conditions for microgravity experiments delineating the microsegregation, observation of convecto-diffusive instabilities and comparison with theoretical models. The overall objectives can be summarized as follows:

- Observe and study the double diffusive and morphological instabilities in controlled conditions and to compare with theoretically predicted convective and morphological instability curves.
- Study the three dimensional morphological instabilities and resulting cellular growth that occur near the onset of morphological instability in the bulk samples under purely diffusive conditions.
- Understand the micro-and macro-segregation of silver dopant in lead bromide crystals in microgravity.
- Provide basic data on convective behavior in alloy crystals grown by the commercially important Bridgman crystal growth process.

2. NECESSITY OF MICROGRAVITY:

Lead bromide doped with silver can be grown under normal gravity conditions, the double diffusive nature of the convection will cause mixing of the molten charge material. This in turn will cause the solute composition in the crystal to constantly increase during growth. In semiconductor devices, where the electronic properties are a function of the crystal composition, this constant compositional variation is undesirable.

During the solidification of doped materials in Bridgman geometry, generation of destablizing temperature gradients in the melt is unavoidable, resulting in buoyancy-induced convective mixing of the liquid phase. On earth this mixing is generally very intensive and prevention of convection is important in order to minimize micro- and macro-segregation and to obtain homogeneous properties throughout the solidified material. In an actual furnace it is extremely difficult to eliminate the radial temperature gradient completely. Unavoidable gradients may give rise to flows which lead to lateral segregation in the solidified material. In binary systems, if the solute pile up ahead of the solidification front is lighter than the solvent, this would cause a positive density gradient. The net density gradient can have various profiles, depending on the properties of the melt such as thermal conductivity and diffusion coefficient or growth conditions such as growth rate and thermal gradient. Even if the net resulting temperature gradient is stable, convection can occur due to double diffusive character of solute and temperature with different diffusivities. While there have been many observations on earth of this phenomena in thin samples where convection is not important, it is nearly impossible to study three-dimensional instabilities in bulk samples on earth under purely diffusive conditions. The space experiment on transparent lead bromide-silver bromide alloys would permit a study of the various three dimensional morphologies that occur near the onset of morphological instability. Since the lead bromide-silver bromide system is transparent, experiments in space would allow the direct observation of morphological instability and the resulting cellular growth.

The present experiment on lead bromide-silver bromide alloys permits a study of various three dimensional morphologies that occur near the onset of morphological instability in a bulk crystal. Being able to see exactly what is happening during growth in low earth orbit makes this a unique system for microgravity experimentation. The system chosen here has dual advantages: (a) lead bromide is a transparent system almost ideally suitable for direct in situ observations to study solid-liquid interface phenomena and (b) lead bromide holds great promise for technological applications of acousto-optic devices and narrow band ultraviolet filters.

3. SIGNIFICANT RESULTS:

The solidification experiments with $PbBr_2$-AgBr alloys (500 and 5000ppm) showed double-diffusive instabilities at the solid-liquid interface. When the sample was held stationary, any convection present in the liquid was attributed to the radial heat losses. A systematic observations below the morphological breakdown (Fig.1) at the interface showed the development of the depression which finally ends in interfacial breakdown. When we repeated this experiment with pure lead bromide at a speeds of 2.5 cm/day the interface remained flat and did not show any instabilities. This is consistent with the predicted curve shown in figure 2. The interface got depressed in the center and then slowly formed the instability. As a function of time, the instability developed with a much larger amplitude. When the translation velocity was increased, the interface started breaking down. The flow pattern observed in the $PbBr_2$-AgBr system can be described as a "toroidal roll".

Morphological Stability
Lead Bromide–Silver Bromide Alloys

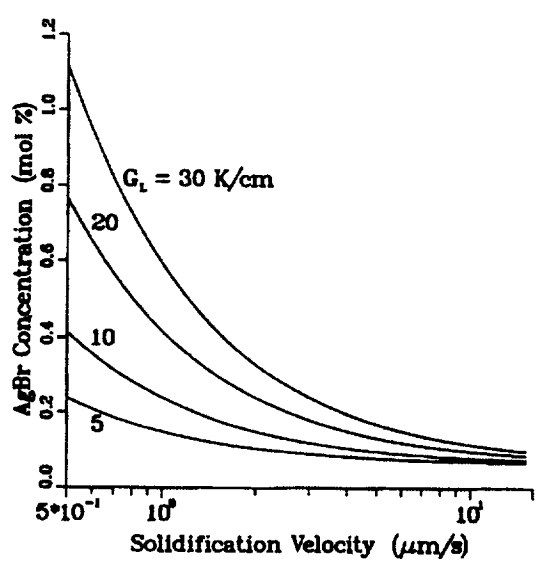

Figure 1 Predicted morphological stability curve for lead bromide-silver bromide system

A slight asymmetry of the system resulted in the displacement of the node and axis of the tours from the central axis of the tube. When the toroidal flow persisted for many hours and the tube was moving, the interface was observed to be pinched where the radial inflow converged leading to the line defect.

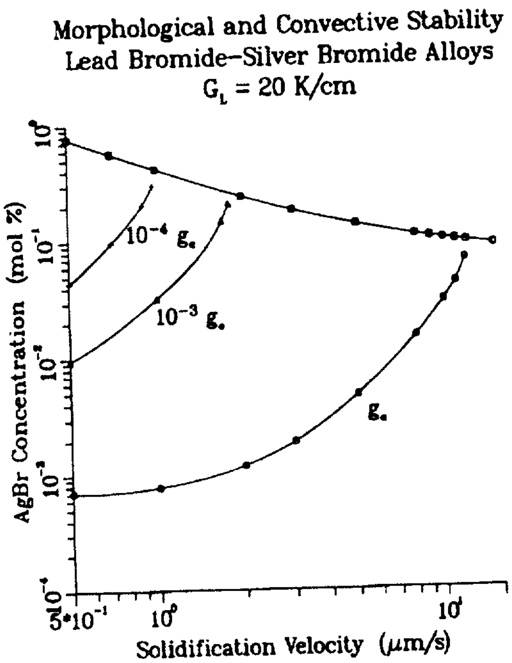

Figure 2 Morphological and convective stability curve for lead bromide-silver bromide system.

A theoretical calculation was performed (Fig. 3) to generate the concentration profile for the solute distribution and we are comparing with the experimentally measured values. We measured the diffusion coefficient and thermal conductivities of solid and liquid which were used in computing stability curves and solute distribution in the crystal. The theoretical composition profiles were calculated for the two bounding cases for 2 growth rates. Both cases assumed a crystal 8 cm in length with .5 % Ag. The diffusion coefficient is 1.7 x 10^{-5} cm^2 /s, and the k value is 0.16. The results are shown in figure 3 for the growth rate of 2 cm/day.

The first case is the well mixed solution where the composition of the liquid at the interface is identical to the composition of the rest of the liquid due to the convective mixing in the liquid. This solution gives a constantly increasing level value for the composition of silver. The second, more desirable case, is the diffusion controlled solution. Here due to a lack of mixing in the liquid, the composition at the interface is different than in the rest of the liquid. The leads to the potential of having a uniform composition of the middle portion of the crystal. Due to the slow growth rate used, the compositional boundary layer will hit the top of the crystal before the steady state composition is reached. This accounts for the jump in the composition profile seen in the 2 cm/day case.

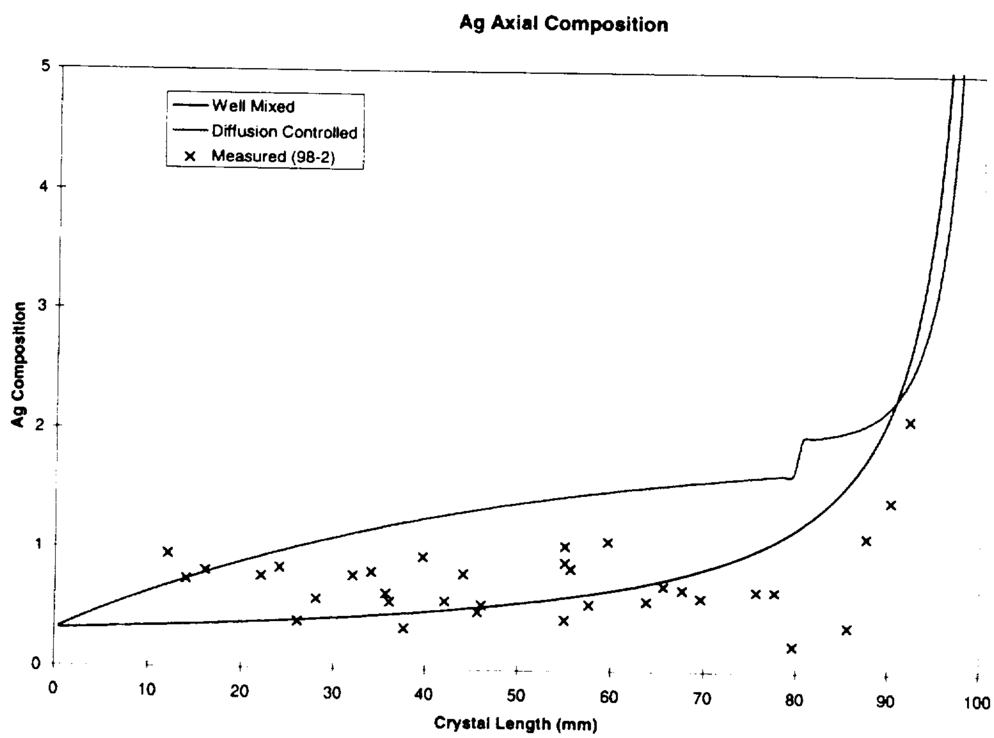

Fig. 3 Calculated and experimentally measured concentration of silver in lead bromide crystals

4. SUMMARY

Direct observations were taken during crystal growth of lead bromide samples doped with 500, 5000 and 10000 ppm silver bromide in 1-g conditions. Stationary solid-liquid interface was flat. When we started growth by moving the ampoule at a velocity lower than critical velocity of interface breakdown, the interface got depressed and the shape of depressed pit varied with the velocity. It became sharply pointed and then slowly formed the instability pulling down the central part of the interface. When the translation rate was increased, the interface broke down. The data showed that the theoretically predicted stability curve agrees well with experimentally observed values. The flow patterns can be described as a toroidal rolls.

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