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Application of a rotating heat field in Bridgman–Stockbarger crystal growth

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Abstract

This note reports the use of heat field rotation as a contact-free influence upon the heat-mass transfer processes in vertical Bridgman–Stockbarger crystal growth. The modified heating furnace which allows the creation of a rotating heat field with various amplitude–frequency characteristics is described. A high-quality, conical, single crystal of $AgGaS_2$ of 30 mm diameter and 80 mm length was grown using this heat field rotation method (HFRM).

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1. Introduction

The vertical Bridgman–Stockbarger method (VBS) is widely used for bulk crystal growth due to its comparative simplicity. The need to reproducibly grow more perfect crystals has provoked attempts to optimize process control of crystal growth. A regime of convection in the fluid phase is likely to be the major factor which controls radial and axial segregation in the growing crystal and is mainly affected by thermal conditions.

Tilting and noncentral positioning of the ampoule, nonsymmetrical temperature distribution at the outer ampoule surface and instabilities in thermoregulation cause nonuniform convective flows, which in turn generate variations in distribution of the segregating components in the growing crystal [1,2]. These problems have resulted in the development of new approaches influencing the convection by the use of controlled flows. These should remedy some of the imperfections of the crystal growth process mentioned above.

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Approaches can be divided into two main groups. The first includes different techniques for mechanical melt stirring (e.g. accelerated crucible rotation (ACRT) and coupled vibration stirring (CVS)), which are achieved by contact influence. The use of external forces is an effective way to optimize growth conditions. Stable and rotating magnetic fields represent the second group of approaches, i.e. contact-free influence through physical fields.

In this work we present another type of contact-free influence on the melt flows—heat field rotation applied to VBS. The heat field rotation method (HFRM) was suggested and developed in the Crystal Growth Lab of the Institute of Mineralogy and Petrography SBRAS [3]. The main idea of the HFRM is the controllable variation of the maximal radial temperature gradient inside the liquid by means of distortion of the heat field from its cylindrical symmetry.

Distortion can be obtained by the partial overheating of the vessel's wall. After that, the rotation of the heat field is attained through the gradual displacement of the overheated zone around the vessel, resulting in the rotation of the maximum temperature gradient around the axis of the vessel and the creation of the so-called thermal wave inside the liquid phase. The magnitude of the azimuthally moving thermal wave depends on the overheating in comparison with the environment, arc size of the overheated zone and its rate of displacement. For instance, if the displacement was very fast, the heat field would appear to retain cylindrical symmetry. Also, the symmetry of the rotating heat field can be varied by means of different sets of the overheated zones around the vessel. Extra effects of the HFRM in the case of VBS configuration will be discussed below.

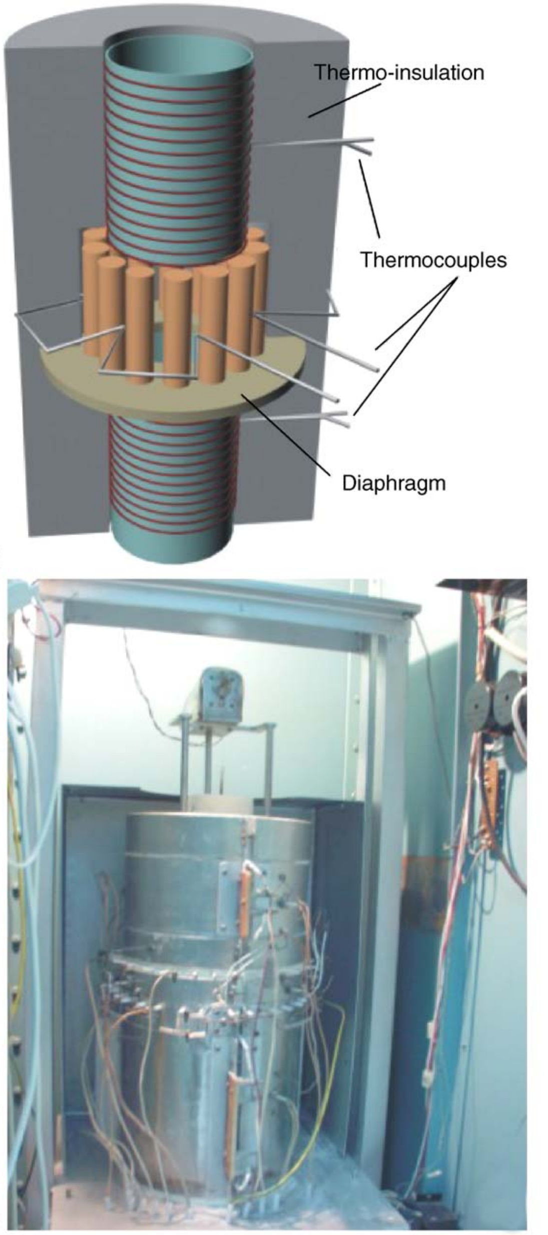
Utilization of the HFRM to the VBS seems to be promising in the case of crystal growth of semiconductors which are known to have a maximum melting point shifted from stoichiometric composition [4]. It is difficult to find the congruent composition so the growth is most likely to proceed from the solution-melt. Hence the maximum homogeneity of such a solution-melt during solidification becomes a key factor in high-quality crystal growth.

2. Description of the setup for applying heat field rotation to VBS

The design of the VBS apparatus evolved mainly from that used in hydrothermal experiments under heat field rotation conditions [5]. The furnace (Fig. 1) consists of three separate heating zones. Upper and lower zones are of standard design, i.e. made by heating wire wrapped around the ceramic tubes. The middle zone is responsible for the heat field rotation in the solidifying melt and is composed of 14 vertically aligned heating elements connected two by two in seven heating groups. The heaters are switched through current leads located outside the furnace (Fig. 2). A parallel Pt–Pt/10% Rh thermocouple consisting of seven working junctions, each of which is placed between two groups of heaters, is used as a temperature sensor. Identical conductors of the thermocouple wires are connected by welded junctions outside the furnace. The resulting emf of such a thermocouple is equal to the average value of the emfs of seven individual thermocouples whose junctions were placed at the same sites. The switchboard distributes the power supply signal from thermoregulator to the heating groups in accordance with the configuration provided by a switch controller.

The rotation of the heat field is attained through the following procedure. The first is the distortion of the heat field from its cylindrical symmetry by switching off certain groups. For example, if we want to form a heat field with symmetry of first order (L_1), one group must be switched off. Finally, the rotation is realized by sequential switching off the adjacent group and switching on the current one. Here, the symmetry of the rotating heat field can be varied by means of different sets of the heated groups switched off at the same time.

The period between switching appears to be the main parameter governing the rate of distortion. Fig. 3 presents the measured amplitudes of periodic temperature oscillations versus the period between the switching of heating groups. The temperatures were measured in a model ampoule provided with quartz tubes for moving the thermocouple along the center and interior wall of the ampoule. The rotating heat field of the first



(a)
(b)

Fig. 1. The Scheme of VBS furnace applied with HFRM (a) and its external view (b).

order (rotL_1) was characterized, i.e. the movement of the single overcooled zone created by one switched off heating group was used. As can be seen, by varying the frequency of switching, appropriate amplitudes of the temperature oscillations could be produced.

Two aspects of HFRM influence to VBS can be assumed:

1. The creation of the two types of axial gradient in the melt (Fig. 4). On the one hand, there is a stabilizing gradient close to the so-called overcooled ampoule wall (profile 1) as an effect of temperature increasing upward in the melt. On the other hand, there is a destabilizing gradient close to the overheated wall (profile 2) which was shown to provide improved radial segregation as compared to the stabilizing configuration [6]. Here, the destabilizing gradient is of the same origin as that created by a short heating booster near the growth interface as described in Ref. [7]. Two different types of axial gradient are likely to produce strong one-vortex convection in the melt directed along the vector of maximal radial temperature gradient. It may result in decreasing the diffusive layer width on the melt–solid interface.

2. The switching of the elements causes the rotation of the maximum temperature gradient in the melt. That will stimulate the azimuthal rotation of the convective cell following the displacement of the overheated zone producing the better mixing of solidifying melt (Fig. 5). Also the increased radial temperature gradient at the melt surface increases the Marangoni convection.

It must be noted that the movement of the solid–liquid interface under imposed temperature oscillations becomes transient during the whole period of growth. The latent heat has a strong effect on the velocity amplitude [8] as well as the thermal diffusivity, so the choice of the optimal period between switching of the heating elements appears to be individual for each material.

3. AGS single-crystal growth using HFRM

In spite of discoveries of many IR materials with high figures of merit for nonlinear applications, $AgGaS_2$ (AGS) still has not lost its importance for optical parametric oscillator and difference frequency generator systems [9].

The experiments of silver thiogallate ($AgGaS_2$) crystal growth under heat field rotation condition

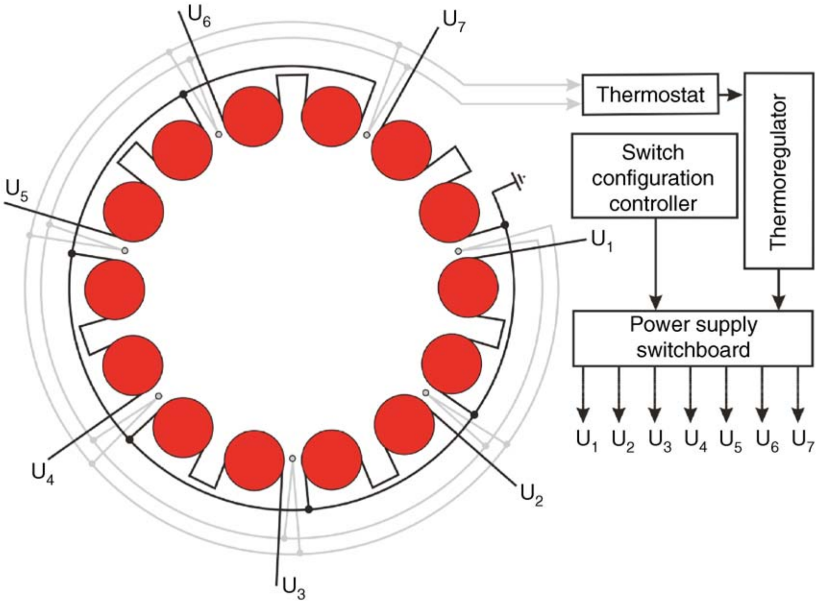


Fig. 2. Temperature control system of the middle zone.

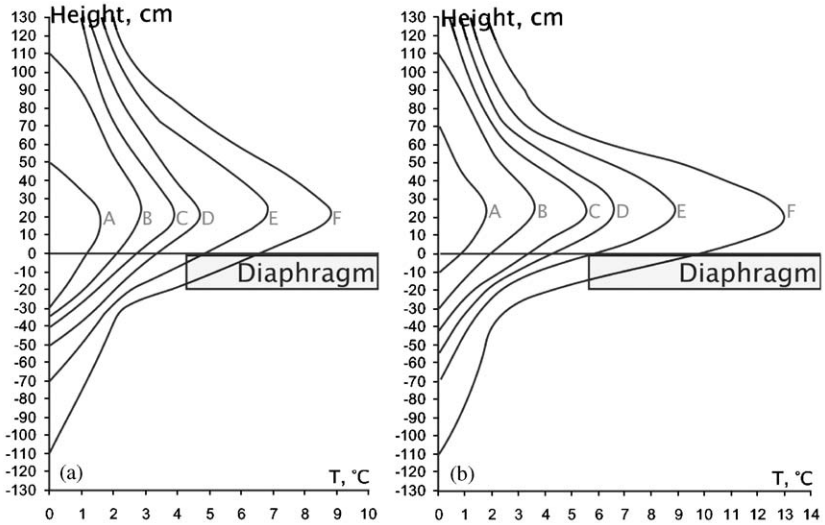


Fig. 3. Measured temperature oscillations (a) along the interior wall and (b) along the center of the model ampoule versus period between the switching of heating groups: A—20 s, B—30 s, C—40 s, D—60 s, E—70 s, F—80 s.

had been carried out. The synthesis procedure from Ag, Ga and S with a nominal purity of 99.999% was the same as described in Ref. [10]. Stoichiometry with a slight excess of Ag_2S and sulfur was chosen as an initial composition in order to account for vacuum evaporation of the melt. The synthesized charge was placed in the quartz conical ampoule coated with pyrolitic

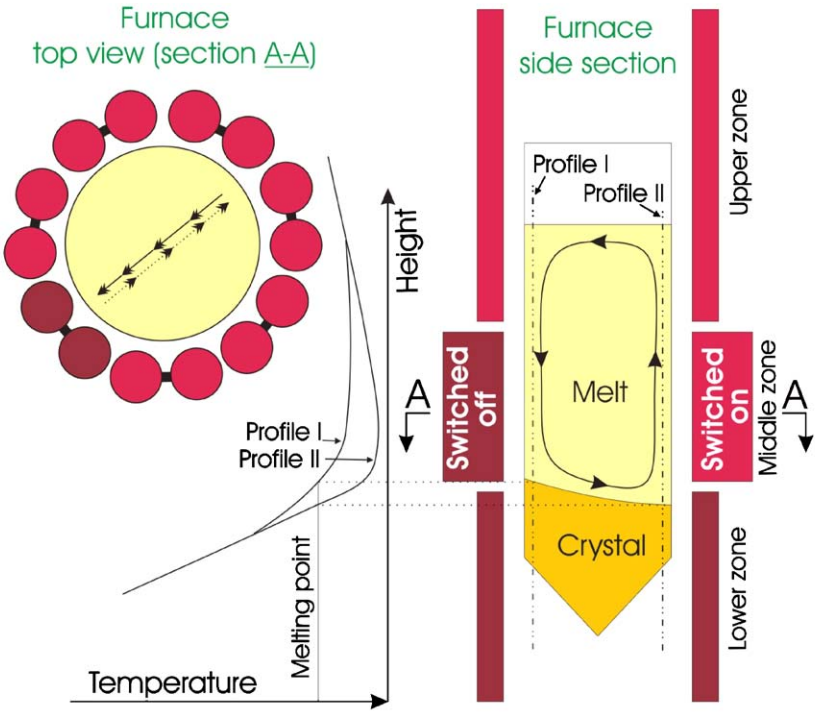


Fig. 4. Two different axial temperature gradients arising along the opposite walls of the ampoule. The heat field has a symmetry L_1.

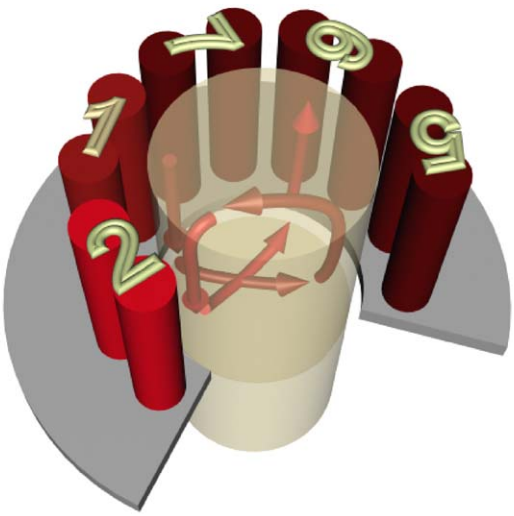


Fig. 5. Rotation of the convective cell as an effect of passing the switched off mode from first to second heating group.

carbon. The ampoule was sealed in another one under 10^{-5} Torr. The growth occurred under rotating heat field with the L_1 symmetry. In order to reach a better uniformity of the melt, the melted charge was exposed to a homogenization procedure using a large period between switching. It corresponds with the temperature oscillations on the ampoule wall near the growth interface equal to 13 °C. Growth rate and axial temperature gradient at the melting point of $AgGaS_2$ was 5 mm/day and ~15 °C/cm, respectively.

The great dependence of crystal quality on the period between switching was observed. Large periods of switching during the growth process produced thermal stress in the crystal, resulting in the formation of many cracks. A crystal of 30 mm diameter and 80 mm length was obtained under a frequency of heat field rotation equal to $1/210\,s^{-1}$ (Fig. 6). Temperature oscillation on the ampoule wall reached values of about 3 °C. The crystal shows the absence of Ag_9GaS_6 interior precipitates [11] and microscopic flakes often observed in annealed crystals grown in stabilized and uniform heat fields. The absence of cracks, twins and interior gas bubbles makes it suitable for the fabrication of nonlinear optical elements.

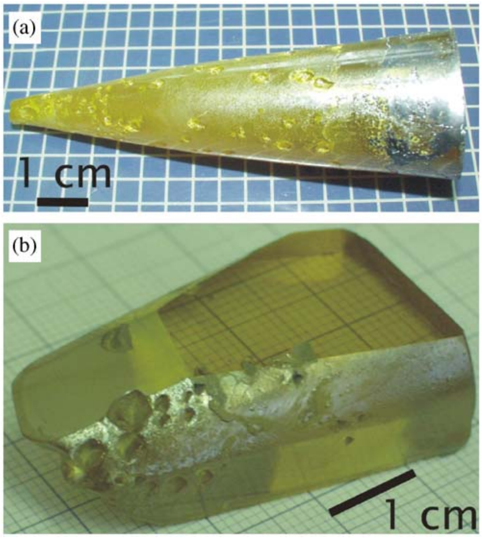


Fig. 6. As-grown $AgGaS_2$ single crystal under heat field rotation conditions (a) and annealed plate of 15 mm width (b).

4. Conclusions

Heat field rotation is a promising new variation on single-crystal growth by the VBS technique. The furnace described has significant capabilities of thermal field parameters for optimizing the technological process of crystal growth. High-quality $AgGaS_2$ crystals confirm the supposition that periodic temperature oscillations near the growth interface favour the convective regime in the melt.

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