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Modeling effects of solute concentration in Bridgman growth of cadmium zinc telluride

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ABSTRACT

Numerical modeling is used to investigate the effect of solute concentration on the melt convection and interface shape in Bridgman growth of $Cd_{1-x}Zn_xTe$ (CZT). The numerical analysis is compared to experimental growth in cylindrical ampoules having a conical tip performed by Komar et al. (2001) [15]. In these experiments, the solidification process occurs at slow growth rate ($V = 2{\cdot}10^{-7}$ m/s) in a thermal field characterized by a vertical gradient $G_T = 20$ K/cm at the growth interface. The computations performed by accounting the solutal effect show a progressive damping of the melt convection due to the depleted Zn at the growth interface. The computed shape of the crystallization front is in agreement with the experimental measurement showing a convex-concave shape for the growth through the conical part of the ampoule and a concave shape of the interface in the cylindrical region. The distribution of Zn is nearly uniform over the crystal length except for the end part of the ingots. The anomalous zinc segregation observed in some experiments is explained by introducing the hypothesis of incomplete charge mixing during the homogenization time which precedes the growth process. When the crystallization is started in ampoules having a very sharp conical tip, the heavy CdTe is accumulated at the bottom part of the melt, giving rise to anomalous segregation patterns, featuring very low zinc concentration in the ingots during the first stage of the solidification.

1. Introduction

Cadmium zinc telluride (CZT) is the most important semiconductor used as substrate in infrared imaging devices. CdZnTe crystals are also used for producing X-ray and γ-ray detectors. The main problem in Bridgman growth of these crystals is the low structural quality and the compositional non-homogeneity of the ingots.

Controlling the shape of the solid–liquid (SL) interface is one of the most important features in melt crystal growth processes. Experimental studies [1,2] in agreement with the predictions of Kuppurao and Derby [3] have shown that promoting convex shapes of the SL interface at the beginning of the growth process by adding a high thermal conductivity pedestal, can improve the crystal quality. By contrast, a concave shape of the interface generates a multiple grains structure of the ingots, due to the propagation of defects from the crucible wall to the sample center [4].

Several papers [5–12] have been dedicated to numerical modeling of the Bridgman growth of CdTe and CdZnTe. In their work, Kuppurao et al. [5,6] performed a detailed analysis of the heat transfer, melt convection and Zn segregation during vertical Bridgman growth of CdZnTe. Other numerical studies [7,8] have been dedicated to the analysis of the growth process of CdTe in cylindrical ampoules with different tip geometries. Gasperino et al. [9] and Lun et al. [10] studied the shape of SL interface during the growth of CdZnTe in electrodynamic gradient freeze (EDG) furnace. They found better conditions for the growth with a slightly convex interface in the cone region of a pyrolytic boron nitride (PBN) crucible [9]. However, engineering the shape of the growth interface by controlling the temperature gradients in EDG furnaces is difficult, since the sensitivity of the interface shape decreases in high-gradient systems [10]. More recent studies [11,12] have been dedicated to the optimization of the thermal furnace profile in order to maintain a convex shape of the interface during the whole growth process in cylindrical ampoules with a conical shape of the tip.

The segregation of zinc has been experimentally and numerically investigated in several papers [13–19]. In their work, Babenstov et al. [13] and Fiederle et al. [14] have demonstrated that the resistivity of CZT correlates with the distribution of Zn in crystals. They found radial variations of zinc concentration up to

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20 percent over the CZT wafers cut perpendicular to the crystal axis. Anomalous segregation featuring an increase in Zn axial concentration during the early stage of the growth process has been observed in some experiments [14–18]. This anomaly was related to a considerable supercooling of the first-to-freeze region of the melt [17–19]. Superheating-supercooling experiments performed in Bridgman ampoules have shown that the crystalline quality of CdTe ingots can be improved if the melt is overheated before the crystallization process [20,21].

The goal of the present work is the numerical analysis of the solutal effect (due to Zn distribution) on the melt convection and the morphological stability of the solid–liquid interface during vertical Bridgman growth of $Cd_{1-x}Zn_xTe$. Numerical computations are compared to experimental Bridgman growth of CZT performed by Komar et al. [15].

2. Model description

The modeling is performed for an axisymmetric domain containing the solid–liquid CZT charge and the graphite ampoule. The system is modeled after the ampoule configuration used to grow CZT crystals in a high-pressure Bridgman furnace [15]. In these experiments, three individual groups of crystals, named S-1, S-2 and S-3, were grown under different thermal conditions. Graphite crucibles having different shapes of the conical tip were used for each series of experiments. The temperature gradient at the growth interface was $G_T \cong 20$ K/cm and the crucible pulling rate $V = 0.5 - 0.8$ mm/h. The nominal Zn content of the charges varies between 10% and 20%.

The geometry of the simulation domain used to model the experiments S-2 and S-3 is shown in Fig. 1. The cylindrical samples have 5 cm in diameter and 7.4 cm in length. The graphite crucibles of 0.2 cm thickness have different shapes of the conical tip. The pulling rate used in the present simulations is $V = 2\cdot10^{-7}$ m/s.

The coupled equations of heat transfer, momentum and species transport are solved by using the finite elements software COMSOL Multiphysics:

$$\rho c_P\left(\frac{\partial T}{\partial t} + \vec{u}\nabla T\right) = k\nabla^2 T \tag{1}$$

$$\rho\left[\frac{\partial \vec{u}}{\partial t} + (\vec{u}\nabla)\vec{u}\right] = -\nabla p + \mu\nabla^2\vec{u} - \rho\vec{g}[\beta_T(T - T_0) + \beta_C(C - C_0)] \tag{2}$$

$$\frac{\partial C}{\partial t} + \vec{u}\nabla C = D\nabla^2 C \tag{3}$$

In the above equations, ρ, c_P, k, p, μ, β_T, β_C, D, T, $\vec{g}$ and $\vec{u}$ are respectively the density, specific heat, thermal conductivity, pressure, dynamic viscosity, thermal expansion coefficient, solutal expansion coefficient, diffusion coefficient, temperature, gravity vector and the flow velocity.

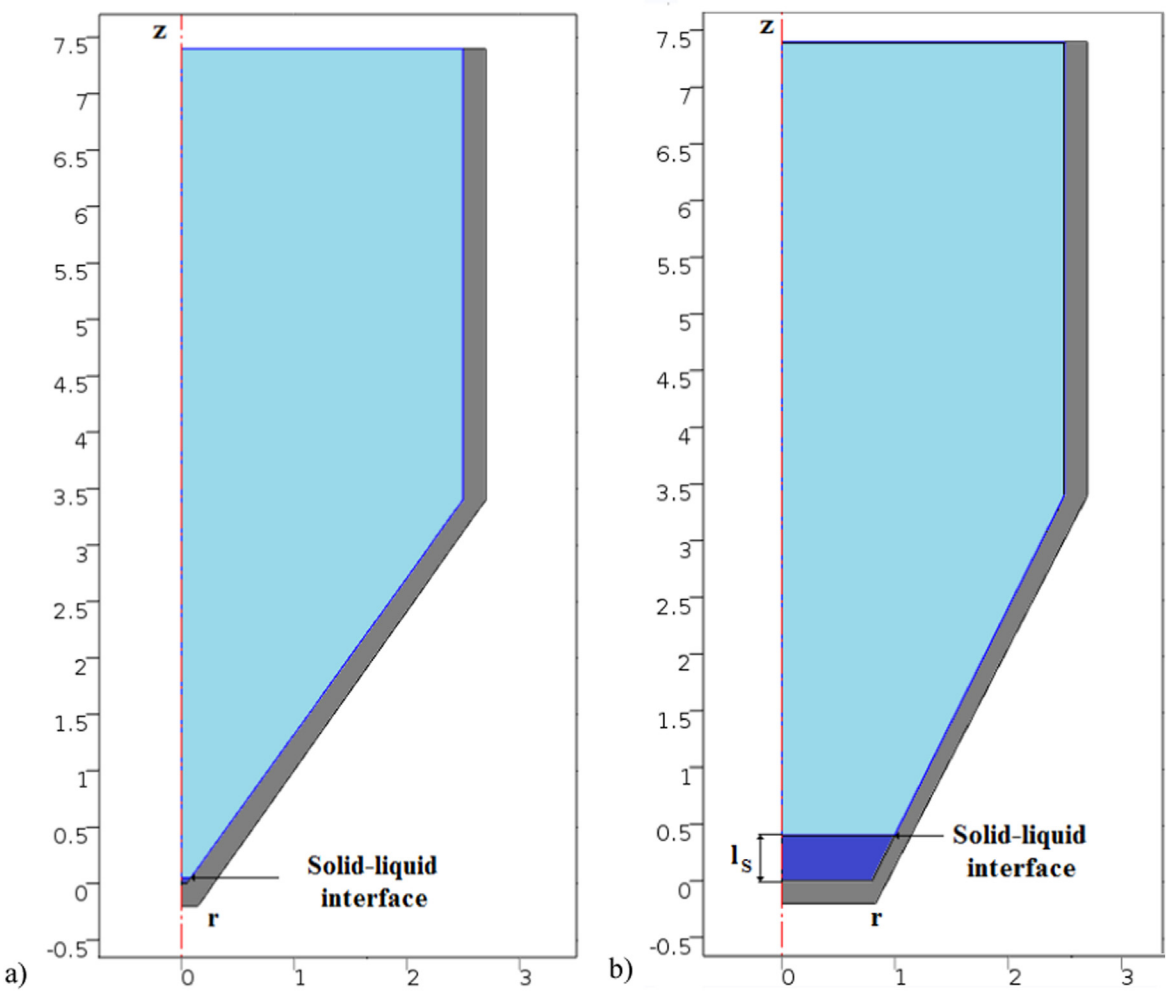

Fig. 1. Geometry of the axisymmetric simulation domain used to model the experiments S-2 (a) and S-3 (b).