



## SIZES OF CRYSTALLITES AS A FUNCTION OF COOLING RATE

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### Introduction

The effective function model of phase transitions (1) has been applied to the process of crystallisation of the segregating solid solutions  $Pb_{1-x}Sn_xTe$  and  $Ge_{1-x}Si_x$  in order to determine the values of the maximum sizes of crystallites and the effective diffusion coefficients for the liquid phase.

The model has already been checked in a number of investigations ((2) and the references herein), but verification of the maximum possible size of a crystallite  $L_{max}$  for a binary system that undergoes a certain rate of temperature drop  $w$  is still lacking. The theory obtains the simple relation (3):

$$L_{max} = \sqrt{\frac{D_l}{Fw}} \quad (1)$$

Here  $w = dT/dt$  with  $T$  denoting temperature and  $t$  the time.  $D_l$  is the effective diffusion coefficient in the liquid and  $F$  denotes the effective intensity function defined by

$$F = \frac{1}{(C_l - C_s)m}$$

$C_l$  and  $C_s$  represent liquidus and solidus point at the crystallisation temperature, respectively, and  $m = dT/dC_l$  is the inclination of the liquidus curve at the same temperature. So  $F$  can be calculated from the phase diagram if the starting temperature of solidification or, equivalent, the melt consistence is known. Eqn. (1) is correct if the crystallisation process is isothermal, i.e. temperature gradients in the system must be negligible.

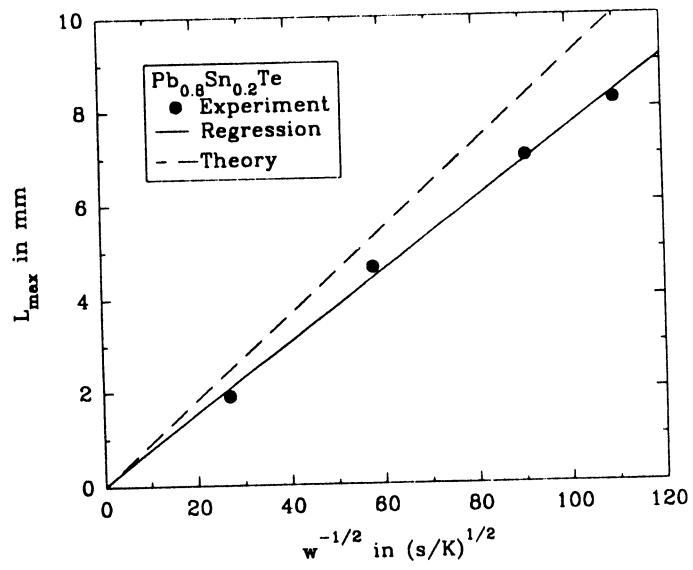


Fig. 1: Maximum crystallite length  $L_{max}$  in  $Pb_{0.8}Sn_{0.2}Te$  as a function of  $w^{1/2}$ .

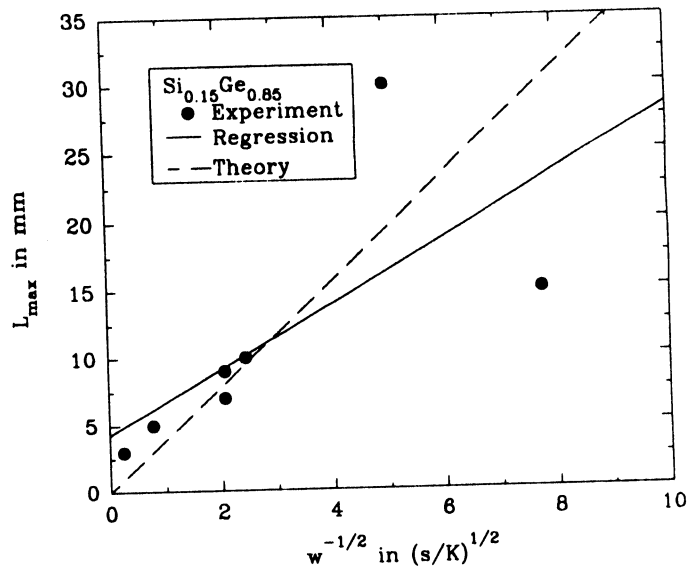


Fig. 2: Maximum crystallite length  $L_{max}$  in  $Si_{0.15}Ge_{0.85}$  as a function of  $w^{1/2}$ .

### Experimental

The idea of this work is an experimental check of Eqn. (1). We performed controlled solidification experiments on the pseudo-binary system  $Pb_{1-x}Sn_xTe$  and looked for the maximum sizes of the crystallites, which developed during the cooling process. Additionally, we analysed data which were independently obtained in an earlier work on the solidification of the solid solution  $Si_xGe_{1-x}$  (4).

Crystallisation of  $Pb_{1-x}Sn_xTe$  with composition  $x = 0.2$  was carried out in a sealed quartz ampoule under isothermal conditions. Cooling rates ranged from  $8 \cdot 10^{-5}$  K/s to  $1 \cdot 10^{-3}$  K/s. Initial temperature in all cases was 1180 K. Grown ingots were sliced and metallographically investigated. Crystallites from the lead-tin/lead-telluride solution were made visible by grinding the wafer surfaces. By means of optical microscopy values of the maximum lateral crystallite size,  $L_{max}$ , and an average length could be determined.

The second investigated system,  $Si_xGe_{1-x}$  with  $x = 0.15$ , was solidified in vacuum-sealed quartz ampoules at rates ranging from  $1.4 \cdot 10^{-4}$  K/s, achieved by programmed cooling up to 17 K/s by quenching in water (4). Samples were cut longitudinally, polished metallographically, and etched. Maximum lengths of segregation structures,  $L_{max}$ , were determined via optical micrographs.

### Results and discussion

Experimentally derived values of  $L_{max}$  vs.  $w^{0.5}$  are shown in Figs. 1 and 2. In Fig. 1 the points for  $Pb_{1-x}Sn_xTe$  lie almost on a straight line. The regression is drawn as a solid line. Eqn. (1) indeed predicts such a behaviour if we assume  $F$  to be constant. The theoretical behaviour of  $L_{max}$  according Eqn. (1) is marked as a dashed line. For this calculation we took  $F$  from the phase diagram (5) and assumed that it has always the value of the starting composition. Values of  $D_i$  were estimated by extrapolation of data given in (5,6). From the three coefficients,  $D_{i,Te}$ ,  $D_{i,Pb}$ , and  $D_{i,Sn}$  only one of them,  $D_{i,Te}$  is known and can be used for comparison. In our case, according to (6) (using extrapolation),  $D_{i,Te} = 9.2 \cdot 10^{-10}$  m<sup>2</sup>/s. Both lines, theory and regression of experimental data are almost parallel with experimental values always below the theoretical curve. However, theory gives the **maximum** size of crystallites which can develop, but because searching only through limited volumes of an ingot and due to the finite number of experiments, error bars are always in the direction of larger sizes. From a linear regression to the experimental points we can derive a value for the diffusion coefficient  $D_i$  as  $6.4 \cdot 10^{-10}$  m<sup>2</sup>/s which indeed represents a good coincidence between experimental and theoretical values for such kind of experiment.

Results of the solidification experiments on  $Si_{0.15}Ge_{0.85}$  are reported in Fig. 2. Data are scattering which may be due to poor statistics, as only one longitudinal cut of every sample was investigated. Also here theory is marked by a dashed line with  $F$  taken from the Si-Ge phase diagram (7) and diffusion coefficient  $D_i = 7.25 \cdot 10^{-8}$  m<sup>2</sup>/s derived from a linear interpolation (8). For high solidification rates sizes of segregating structures are larger than the theory predicts. This may be due to the fact that such a fast crystallization does not occur under isothermal conditions — thus real cooling rates are slower. For low rates there are only two points far away from what is predicted by the theory, therefore nothing concluding can be said. However, we performed a linear regression to the experimental data points and obtained a value for  $D_i$  in  $Si_{0.15}Ge_{0.85}$  as  $6.4 \cdot 10^{-8}$  m<sup>2</sup>/s, which is surprisingly near to the theoretical value.

### Conclusions

We have shown in two examples that the theoretical approach of the effective function theory and especially Eqn. (1), which predicts the maximum sizes of grown crystallites are in a good agreement with experimental results and could also be useful for estimations of one-phase diffusion parameters.

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