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Solubility limits and segregation aspects in the growth of RE³⁺-doped optical bulk crystals

Matias Velázquez

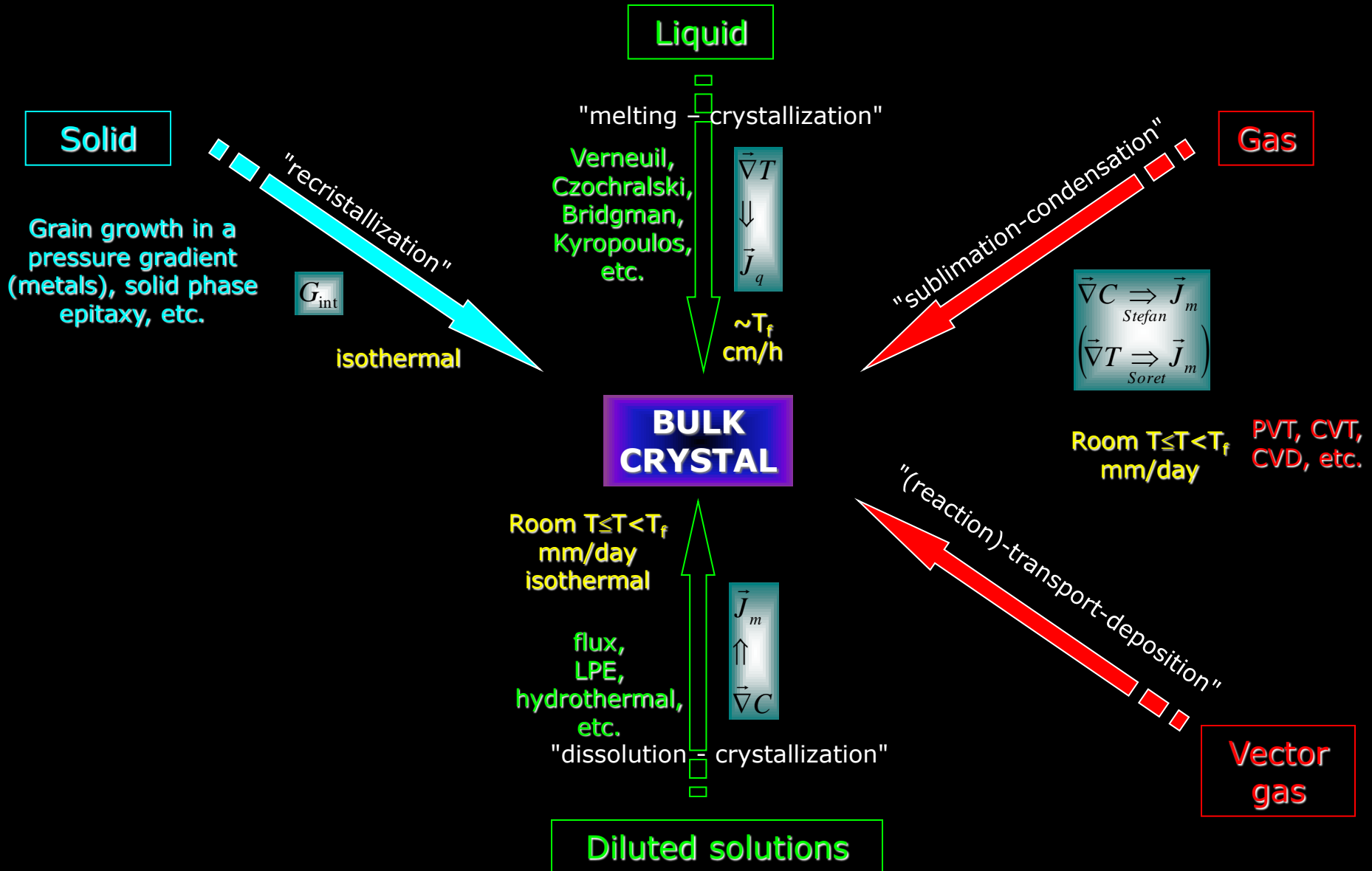
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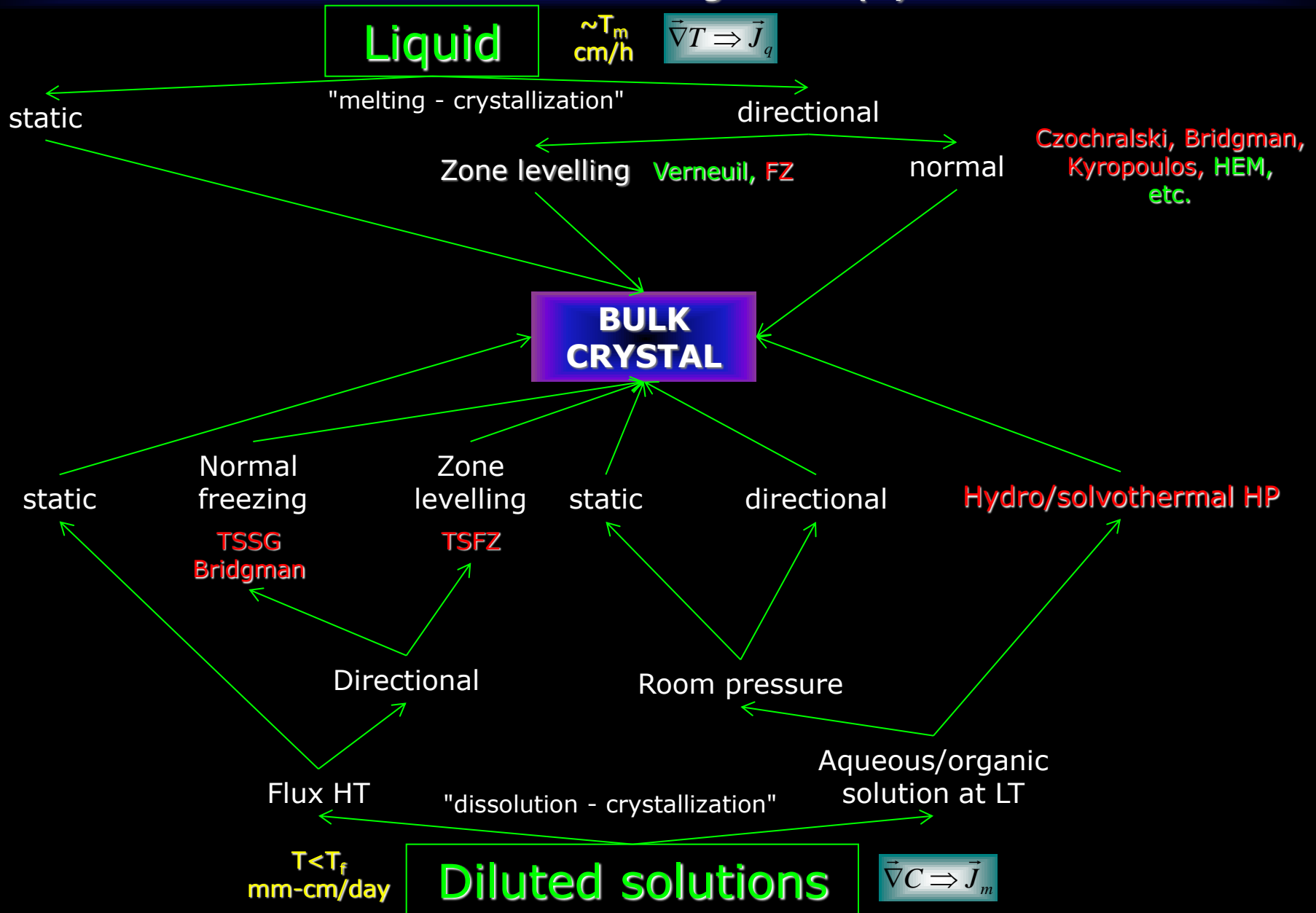


**Marie Curie Initial Training Network
Coherent Information Processing
in Rare-Earth Ion Doped Solids**

General principles of crystal growth : nucleation and growth



General principle of crystal growth : nucleation and growth (2)



Outline

- Equilibrium solubility limit :
 - *Nd³⁺-doped CaWO₄*
 - *Co-doping and association to increase the solubility limit*
 - *Point defects association kinetics in Er³⁺-doped KPb₂Cl₅*
- Equilibrium partition coefficient of Er³⁺ in a Y₂SiO₅ crystal grown from the melt
- Equilibrium partition coefficient of Yb³⁺ in a Gd₂O₃ crystal grown from a Li₆Gd(BO₃)₃ flux
- Dopant concentration profiles in crystals grown from the melt
- Morphological instability of the solidification interface during a crystal growth experiment

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CaWO₄ : longevity record for a scintillating crystal

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Cite this: *CrystEngComm*, 2013, 15, 2301

Growth of high-purity scintillating CaWO₄ single crystals for the low-temperature direct dark matter search experiments CRESST-II and EURECA

Andreas Erb^{*ab} and Jean-Côme Lanfranchi^{bc}



Fig. 4 Cut and polished pieces of the CaWO₄ crystal; from left to right: tail, residual cylinder, detector crystal, shoulder and neck.

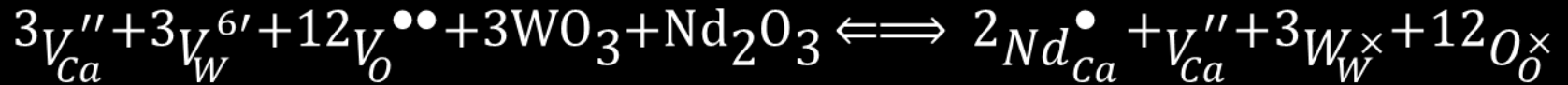


Fig. 5 Three CaWO₄ crystals from subsequent growth experiments weighing 853 g each, demonstrating the high reproducibility of the crystal growth procedure. The crystals at the left and the right are as-grown, while the clear crystal in the middle has already undergone an oxygenation treatment at 1450 °C in pure oxygen atmosphere followed by slow cooling. Note, the near square cross section of the crystals in their cylindrical part, as a result of the growth anisotropy.

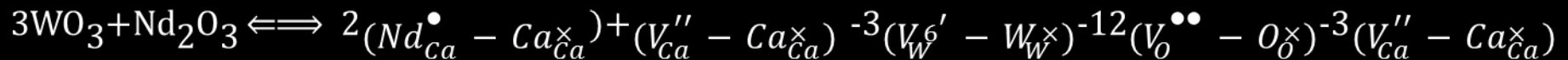


Fig. 2 CaWO₄ crystal of 886 g with seed holder and seed after growth. The slightly grey colour of the crystal is due to an oxygen deficiency originating from the low oxygen partial pressure in the growth atmosphere. The grey colour can be removed by a subsequent annealing procedure in pure oxygen at elevated temperatures.

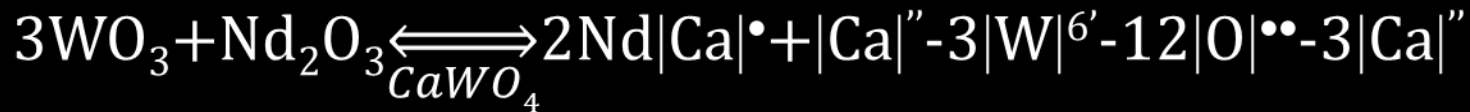
Equilibrium solubility limit : Nd³⁺-doped CaWO₄



Structure elements to building units transformation



Modern Schottky notation for the building units transformation



$$3\mu_{WO_3} + \mu_{Nd_2O_3} \approx 3\mu_{WO_3}^0 + \mu_{Nd_2O_3}^0 = 2\mu_{Nd|Ca|^{\bullet}} + \mu_{|Ca|''} - 3\mu_{|W|^{6'}} - 12\mu_{|O|^{\bullet\bullet}} - 3\mu_{|Ca|''}$$

No mutual solubility



$$3\mu_{CaWO_4}^0 = -3\mu_{|Ca|''} - 3\mu_{|W|^{6'}} - 12\mu_{|O|^{\bullet\bullet}}$$

Schottky's « *Gittermolekül* » to fix the reference state

Equilibrium solubility limit : Nd³⁺-doped CaWO₄ (2)

$$\text{In equilibrium : } 2\mu_{\text{Nd|Ca}\bullet} + \mu_{\text{|Ca|''}} = \mu_{\text{Nd}_2\text{O}_3}^\circ + \mu_{\text{WO}_3}^\circ - 3\mu_{\text{CaWO}_4}^\circ$$

$$\text{Or } \Delta G_d = \Delta H_d - T\Delta S_d = 0$$

$$\Delta H_d = 2\Delta U_{\text{d,Nd|Ca}\bullet} + \Delta U_{\text{d,|Ca|''}} + 2\Delta E_{\text{st,Nd|Ca}\bullet} + \Delta E_{\text{st,|Ca|''}}$$

$$\Delta S_d = 2\Delta S_{\text{xc,Nd|Ca}\bullet} - 2R\ln([\text{Nd|Ca}\bullet]/[\text{CaWO}_4]) + \Delta S_{\text{xc,|Ca|''}} - R\ln([\text{|Ca|''}]/[\text{CaWO}_4])$$

Electroneutrality condition : $[\text{Nd|Ca}\bullet] = 2[\text{|Ca|''}]$

$$x_{\text{Nd|Ca}\bullet}^s = 2^{1/3} e^{(2\Delta S_{\text{xc,Nd|Ca}\bullet} + \Delta S_{\text{xc,|Ca|''}})/3R} e^{[-2(\Delta U_{\text{d,Nd|Ca}\bullet} + \Delta E_{\text{st,Nd|Ca}\bullet}) - (\Delta U_{\text{d,|Ca|''}} + \Delta E_{\text{st,|Ca|''}})]/3RT}$$

**Solid state solubility limit of Nd³⁺ in CaWO₄ crystal \equiv
« subsolidus » equation**

Equilibrium solubility limit : Nd³⁺-doped CaWO₄ (3)

$$x_{\text{Nd|Ca}^\bullet}^s = 2^{1/3} e^{(2\Delta S_{\text{xc,Nd|Ca}^\bullet} + \Delta S_{\text{xc,|Ca}''})/3R} e^{-2(\Delta U_{\text{d,Nd|Ca}^\bullet} + \Delta E_{\text{st,Nd|Ca}^\bullet}) - (\Delta U_{\text{d,|Ca}''} + \Delta E_{\text{st,|Ca}''})/3RT}$$

$$\Delta U_{\text{d}} = \Delta U_{\text{B}} + U_{\text{L,Nd}_2\text{O}_3} + U_{\text{L,WO}_3} - 3U_{\text{L,CaWO}_4}$$

$$\Delta E_{\text{st,Nd|Ca}^\bullet} = 8\pi\text{GrCa}[r_{\text{Nd}} - r_{\text{Ca}} + \alpha(z_{\text{Nd}} - z_{\text{Ca}})]^2$$

$$\Delta E_{\text{st,|Ca}''} = 8\pi\text{GrCa}[r_{\text{|Ca}''} - r_{\text{Ca}} + \alpha(z_{\text{|Ca}''} - z_{\text{Ca}})]^2 \text{ with } \alpha \sim 0.15 \text{ \AA}$$

$$\Delta S_{\text{xc}} = \Delta S_{\text{ph}} + \Delta S_{\text{mag}} + \Delta S_{\text{el}} + S_{\text{Nd}_2\text{O}_3}^{0,\text{f}} + S_{\text{WO}_3}^{0,\text{f}} - 3S_{\text{CaWO}_4}^{0,\text{f}}, \text{ with } \Delta S_{\text{el}} \approx 0$$

Equilibrium solubility limit : Nd³⁺-doped CaWO₄ (4)

At concentrations such that the Boltzmann approximation is no longer valid, it is necessary to generalize Henry's law at the first order, by Taylor-expanding the dissolution enthalpy and excess entropy in composition

$$\begin{aligned} \Delta H_d &\approx \Delta H_d^0 \times (1 - I_H x_{Nd|Ca}^s) \\ &\quad \parallel \\ \Delta S_{xc} &\approx \Delta S_{xc}^0 \times (1 - I_S x_{Nd|Ca}^s) \end{aligned}$$

I_H and I_S are enthalpic and entropic interaction phenomenological coefficients which quantify the change in depth and curvature of the local potential well upon substitution

$$\frac{\ln 2}{3} + \frac{2\Delta S_{xc,Nd|Ca}^{\bullet} + \Delta S_{xc,|Ca}^{''}}{3R} - \frac{\frac{\ln x_{Nd|Ca}^s}{(1 - 2I_S x_{Nd|Ca}^s)} = [2(\Delta U_{d,Nd|Ca}^{\bullet} + \Delta E_{st,Nd|Ca}^{\bullet}) + (\Delta U_{d,|Ca}^{''} + \Delta E_{st,|Ca}^{''})]}{3RT}$$

Solid state solubility limit of Nd³⁺ in CaWO₄ crystal \equiv
 « subsolidus » equation at higher concentrations

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Co-doping and association to increase the solubility limit

- An old question : $\text{CaWO}_4:\text{Ho}^{3+}, \text{Na}^+$, $\text{ZnS}:\text{Pr}^{3+}, \text{Cu}^+$ or Ag^+ , $\text{LiCAF}:\text{Ce}^{3+}, \text{Na}^+$, etc.
- In $\text{CaWO}_4:\text{Ho}^{3+}$ + excess Na^+ , $k_0=0.25 \Rightarrow k_0=0.83$ (K. Nassau *et al.*, J. Appl. Phys., 33 (10) (1962) 3064-3073)

Substitution reactions at equilibrium



+

+

⇌

⇌



$$\Delta G_1^0 < \Delta G_2^0$$

- the two association equilibria are likely to deplete the solid solution in point defects and lead to an increased dissolution of the Nd sesquioxide
- the second equilibrium is much like an acid-base neutralization : the strong "Schottky acid" dissolves the hardly soluble base

Co-doping and association to increase the solubility limit (2)



No mutual solubility and Schottky's « *Gittermolekül* »

$$4\mu_{\text{WO}_3} + \mu_{\text{Nd}_2\text{O}_3} + \mu_{\text{Na}_2\text{O}} \approx 4\mu_{\text{WO}_3}^0 + \mu_{\text{Nd}_2\text{O}_3}^0 + \mu_{\text{Na}_2\text{O}}^0 = 2\mu_{\text{Nd|Ca|}\bullet} + 2\mu_{\text{Na|Ca|}'} - 4\mu_{|\text{W}|^{6'}} - 16\mu_{|\text{O}|^{\bullet\bullet}} - 4\mu_{|\text{Ca}|''}$$

$$4\mu_{\text{CaWO}_4}^0 = -4\mu_{|\text{Ca}|''} - 4\mu_{|\text{W}|^{6'}} - 16\mu_{|\text{O}|^{\bullet\bullet}}$$

Point defects association equilibrium



$$2\mu_{\text{Nd|Ca|}\bullet} + 2\mu_{\text{Na|Ca|}'} = 2\mu_{\text{Nd|Ca|}\bullet\text{Na|Ca|}'}$$

In equilibria : $\mu_{\text{Nd|Ca|}\bullet\text{Na|Ca|}'} = \frac{1}{2} (\mu_{\text{Nd}_2\text{O}_3}^0 + \mu_{\text{Na}_2\text{O}}^0) + 2 (\mu_{\text{WO}_3}^0 - \mu_{\text{CaWO}_4}^0)$

Or $\Delta G_d + \Delta G_a = \Delta H_d - T\Delta S_d + \Delta H_a - T\Delta S_a = 0$

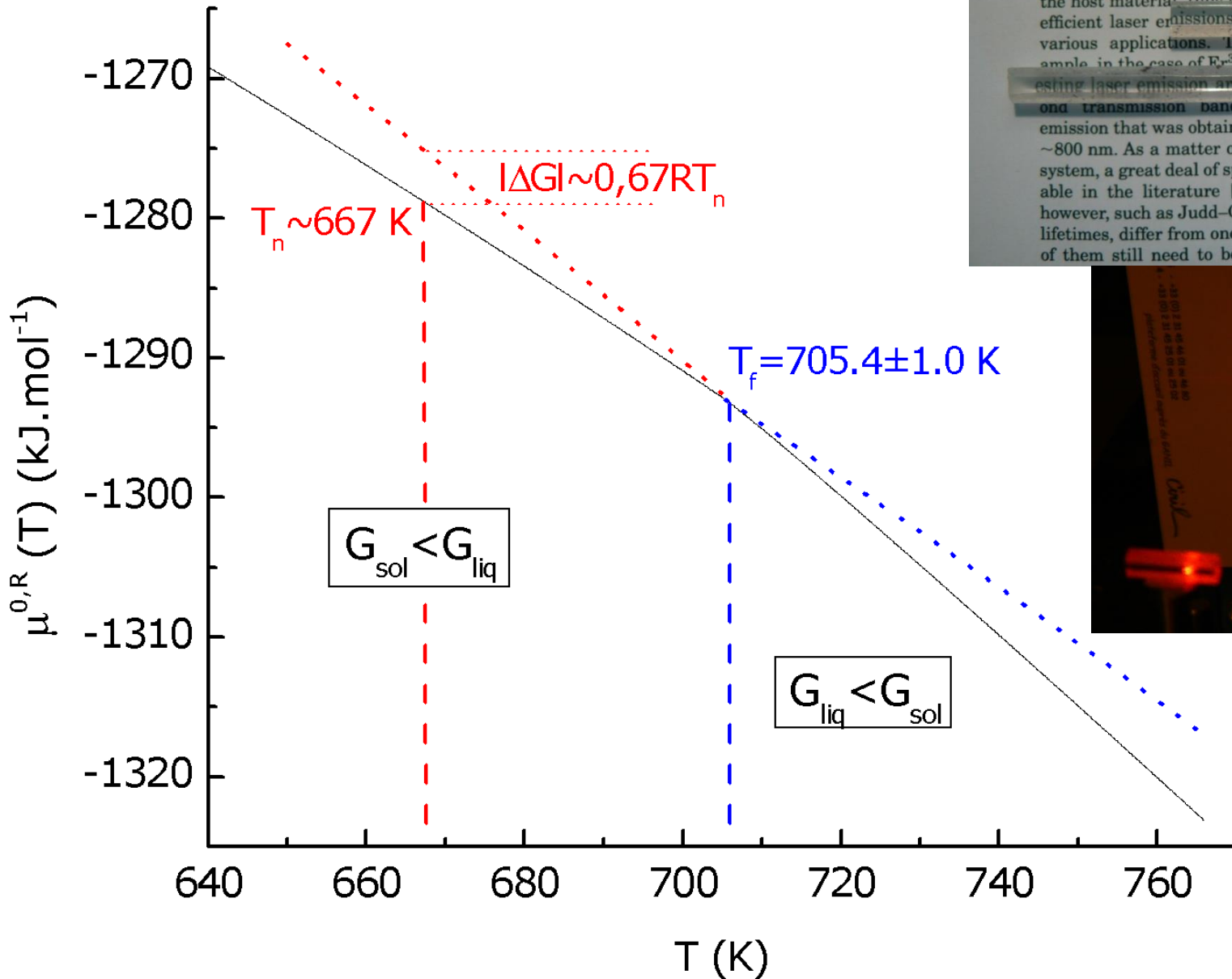
$$x_{\text{Nd|Ca|}\bullet\text{Na|Ca|}'}^s = e^{\left[2(\Delta S_{xc,\text{Nd|Ca|}\bullet} + \Delta S_{xc,\text{Na|Ca|}'}) + \Delta S_{xc,a} \right] / R} e^{\left[-2(\Delta U_{d,\text{Nd|Ca|}\bullet} + \Delta U_{d,\text{Na|Ca|}'}) - \Delta U_a - 2(\Delta E_{st,\text{Nd|Ca|}\bullet} + \Delta E_{st,\text{Na|Ca|}'} - \Delta E_{st,a}) \right] / RT}$$

Associated complex solid state solubility limit

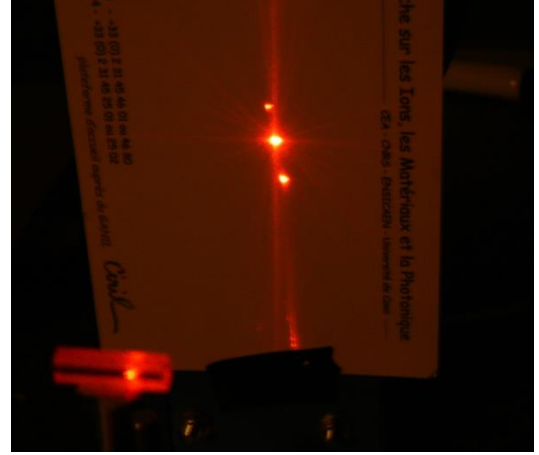
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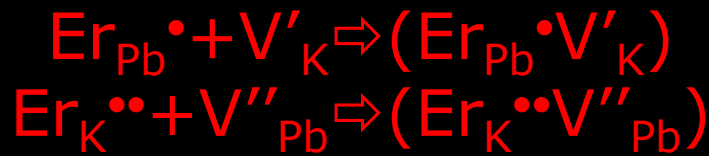
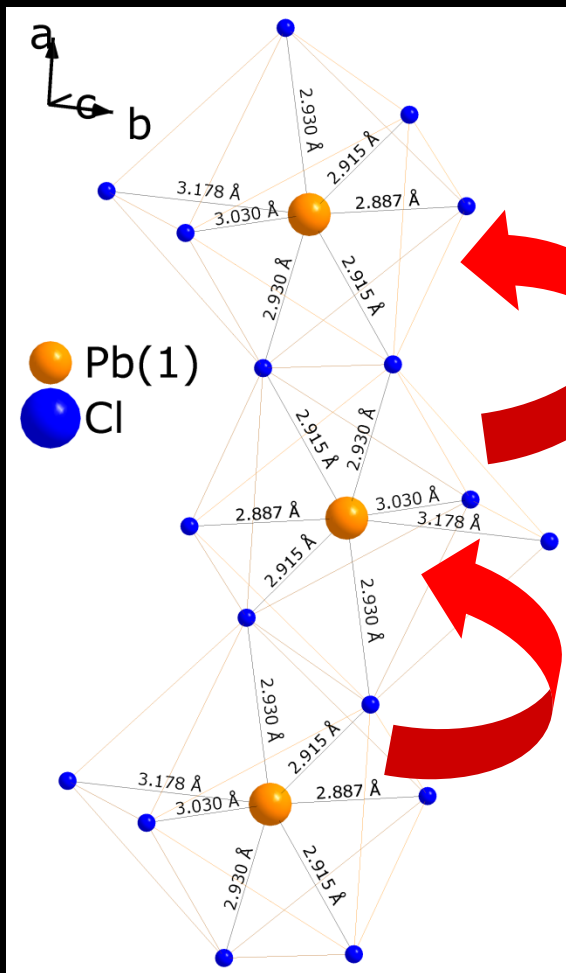
KPb₂Cl₅



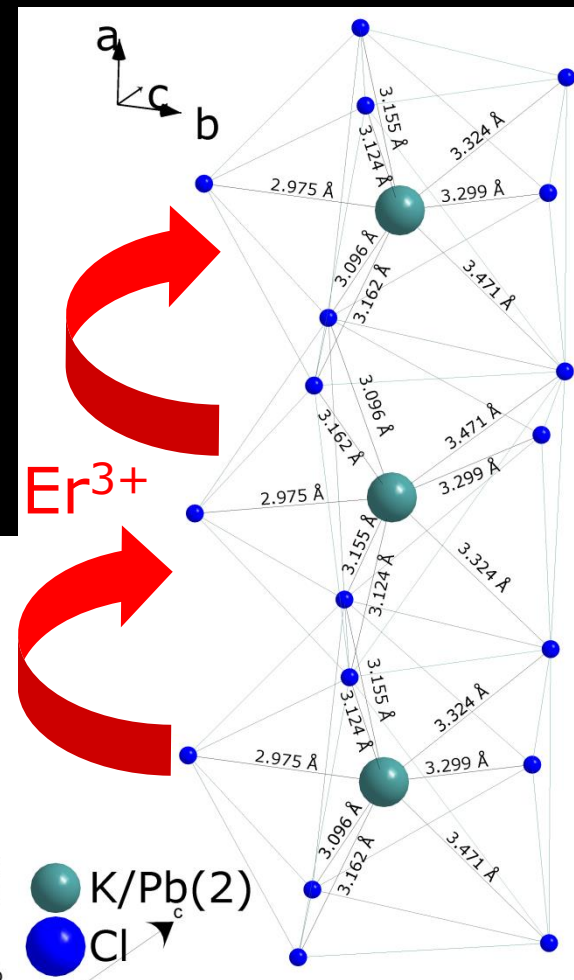
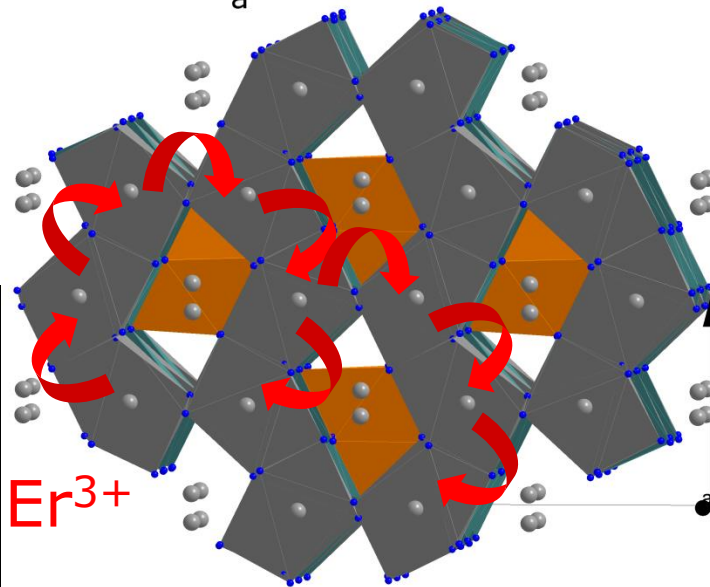
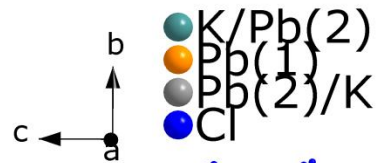
1. INTRODUCTION
Several works have been dedicated in the past years to the growth and the spectroscopic characterization of single crystals of potassium lead chloride KPb₂Cl₅ (KPC) doped with trivalent rare-earth ions [1–11]. This holds in the low phonon energy (203 cm⁻¹), the broad infrared transparency (0.3–22 μm), and the nonhygroscopicity of the host material, thus giving the possibility of obtaining efficient laser emissions in various spectral domains for various applications. This was demonstrated, for example, in the case of Er³⁺-doped KPC, with its very interesting laser emission around 4.6 μm [2], and in the second transmission band of the atmosphere, a laser emission that was obtained under diode-laser pumping at ~800 nm. As a matter of fact, concerning that particular system, a great deal of spectroscopic data is already available in the literature [1,3,5,7,11]. Some of these data, however, such as Judd–Ofelt parameters and fluorescence lifetimes, differ from one reference to the other, and some of them still need to be completed or analyzed further.



Point defects association kinetics in Er^{3+} -doped KPb_2Cl_5



Er^{3+}



Point defects association kinetics in Er³⁺-doped KPb₂Cl₅ (2)

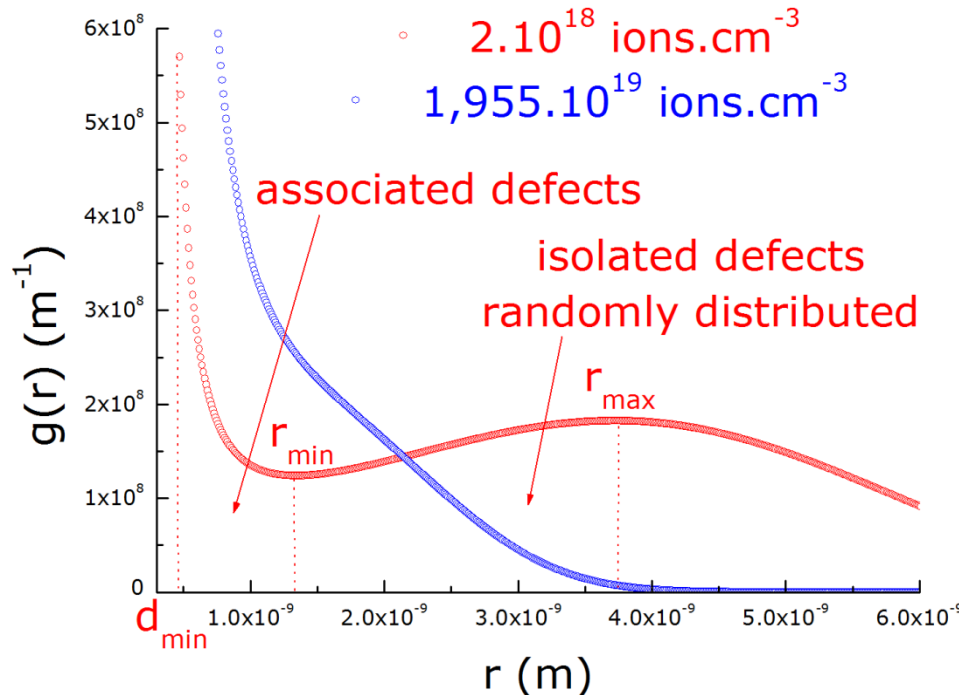
Capture radius

T. R. Waite, J. Chem. Phys., 28 (1) (1958) 103-106

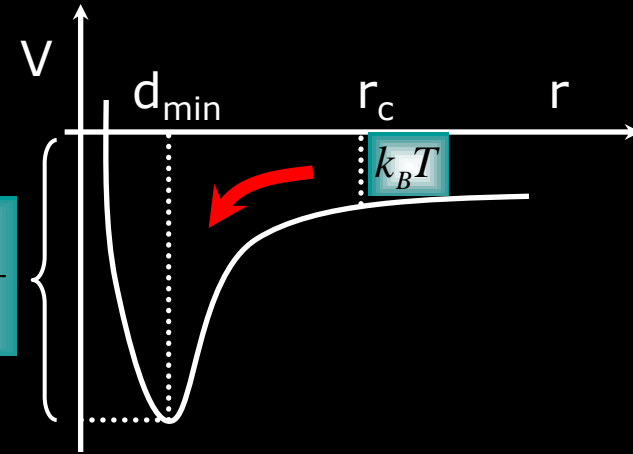
$$r_c = \frac{1}{\int_{d_{\min}}^{\infty} \frac{\exp\left(-\frac{z^+ z^- e^2}{4\pi\epsilon k_B T r}\right)}{r^2} dr}$$

Distribution of the nearest neighbours point defects (Er_{Pb(2)}•V_K)

H. Reiss, J. Chem. Phys., 25 (3) (1956) 400-413



$$\begin{aligned} (\text{Er}_{\text{Pb}(2)} \bullet V_K) r_c(T_f) &\approx 14.1 \text{ \AA} \\ (\text{Er}_K \bullet V''_{\text{Pb}(2)}) r_c(T_f) &\approx 54.1 \text{ \AA} \end{aligned}$$



- $r_{\min} \approx 18.5 \text{ \AA}$ and $r_{\max} \approx 22.1 \text{ \AA} \approx r_{ms} \approx 23 \text{ \AA}$
- $[\text{Er}_{\text{Pb}} \bullet]_i = C_{\infty}$

Radius of a sphere the molecular volume of which equals that of the solute

$$r_{ms} = \left(\frac{3}{4\pi [\text{Er}_{\text{Pb}} \bullet]_i} \right)^{\frac{1}{3}}$$

Point defects association kinetics in Er³⁺-doped KPb₂Cl₅ (3)

$$r_{ms}, r_{\max} > r_c$$

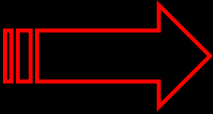
(Pseudo) second order kinetics

T. R. Waite, Phys. Rev., 107 (2) (1957) 463-470

$$\frac{d[Er_{Pb(2)}^\bullet]}{dt} = k(t)[Er_{Pb(2)}^\bullet][V'_K]$$

$$k(t) = 4\pi D r_c \frac{s \left(1 + \frac{\sqrt{\pi D t}}{r_c} \right)}{1 + \frac{(s+1)}{r_c} \sqrt{\pi D t}}$$

Electroneutrality condition in the extrinsic doping regime



$$[Er_{Pb(2)}^\bullet](t) = \left\{ \frac{1}{[Er_{Pb(2)}^\bullet]_i} + \frac{4\pi D r_c s}{s+1} \left[t + \frac{2s r_c}{s+1} \sqrt{\frac{t}{\pi D}} - \frac{2s r_c^2}{\pi D (s+1)^2} \ln \left(1 + \frac{s+1}{r_c} \sqrt{\pi D t} \right) \right] \right\}^{-1}$$

$$r_{ms} < r_c$$

First order kinetics

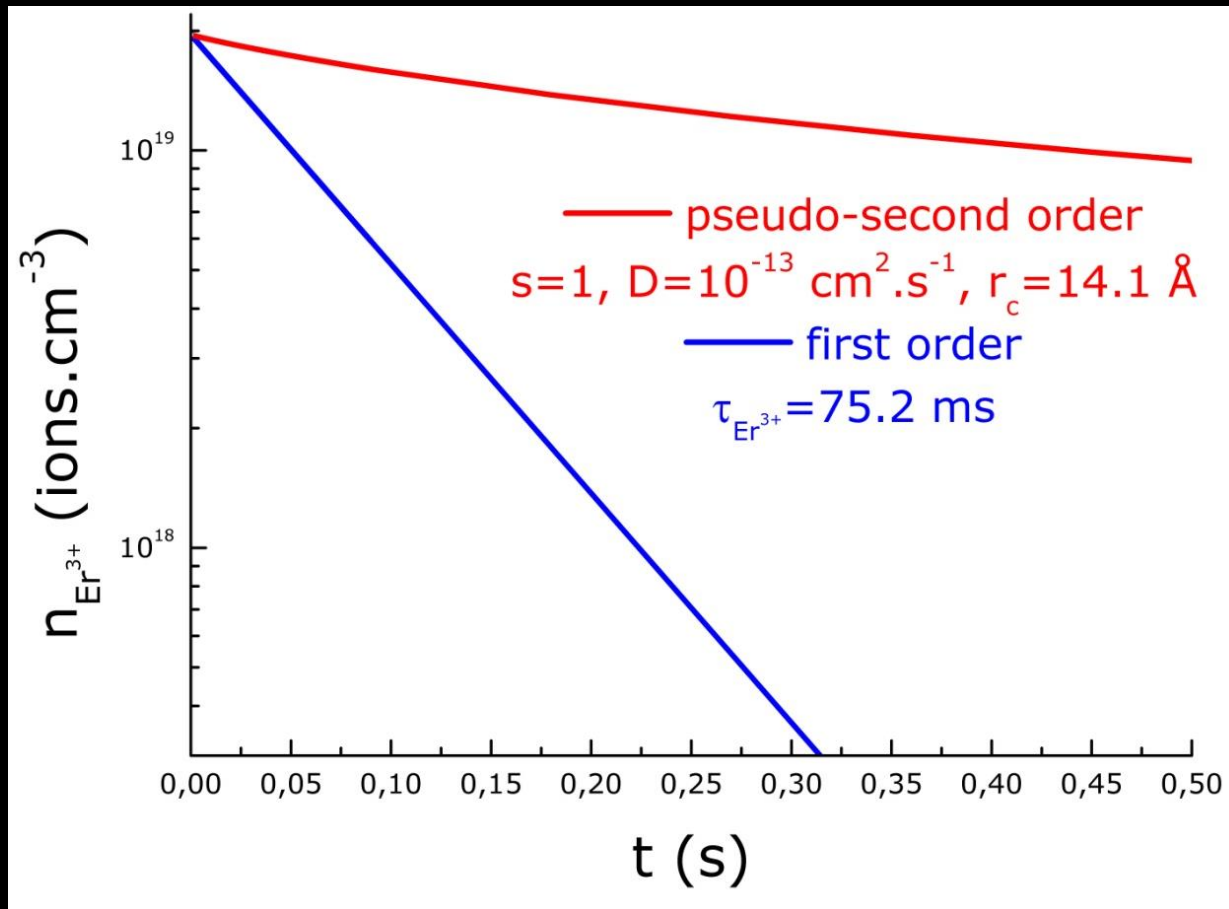
H. Reiss, J. Appl. Phys., 30 (8) (1959) 1141-1152

$$[Er_K^{\bullet\bullet}](t) = [Er_K^{\bullet\bullet}]_i e^{-\frac{t}{\tau_r}}$$

Decay time

$$\tau_r \approx \frac{1}{4\pi f_a [Er_K^{\bullet\bullet}]_i r_c D}$$

Point defects association kinetics in Er^{3+} -doped KPb_2Cl_5 (4)



$$\tau_r(T_f) \approx 0.8 \text{ s}$$

$$\tau_{\text{cool}}(T_f) \approx 26.4 \text{ s}$$

$$\tau_c \sim 10^4 - 10^5 \text{ s}$$

- even in cases where diffusion would be reduced, the isolated ions concentration relaxation time is much lower than the intrinsic cooling time of the crystal and the solidification interface moving time
- as axial and radial segregations affect the r_{ms} , there exists an « elaboration-structure » relationship which might explain discrepancies between results obtained by different authors for a given concentration of dopant in the crystal

Is it a good idea to increase the initial ErCl_3 amount to increase the dissolution of Er^{3+} cations in the KPb_2Cl_5 crystal ?

Er transfer from the liquid phase to the solid phase



- $[\text{Cl}(\ell)] \approx \text{cte}$, $[\text{Cl}_{\text{Cl}}^{\times}] \approx \text{cte}$, $[\text{Er}(\ell)] = C_{\infty}$

$$K = \frac{[\text{Er}_{\text{Pb}}^{\bullet}][V'_K]}{[\text{Er}(\ell)]} = k_0[V'_K]$$

Formation equilibrium of a pair of charged Schottky defects

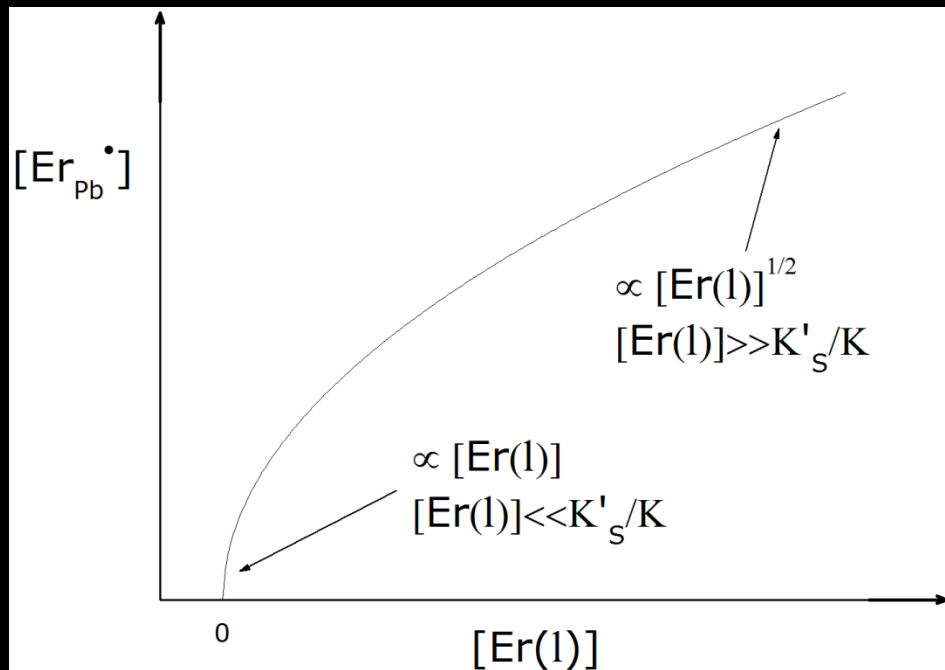
$$K'_S = [V'_K][V_{\text{Cl}}^{\bullet}]$$

Electroneutrality condition in the intrinsic doping regime

$$[\text{Er}_{\text{Pb}}^{\bullet}] + [V_{\text{Cl}}^{\bullet}] = [V'_K]$$

$$k = \frac{\frac{K}{\sqrt{K'_S}}}{\sqrt{1 + \frac{K}{K'_S}[\text{Er}(\ell)]}}$$

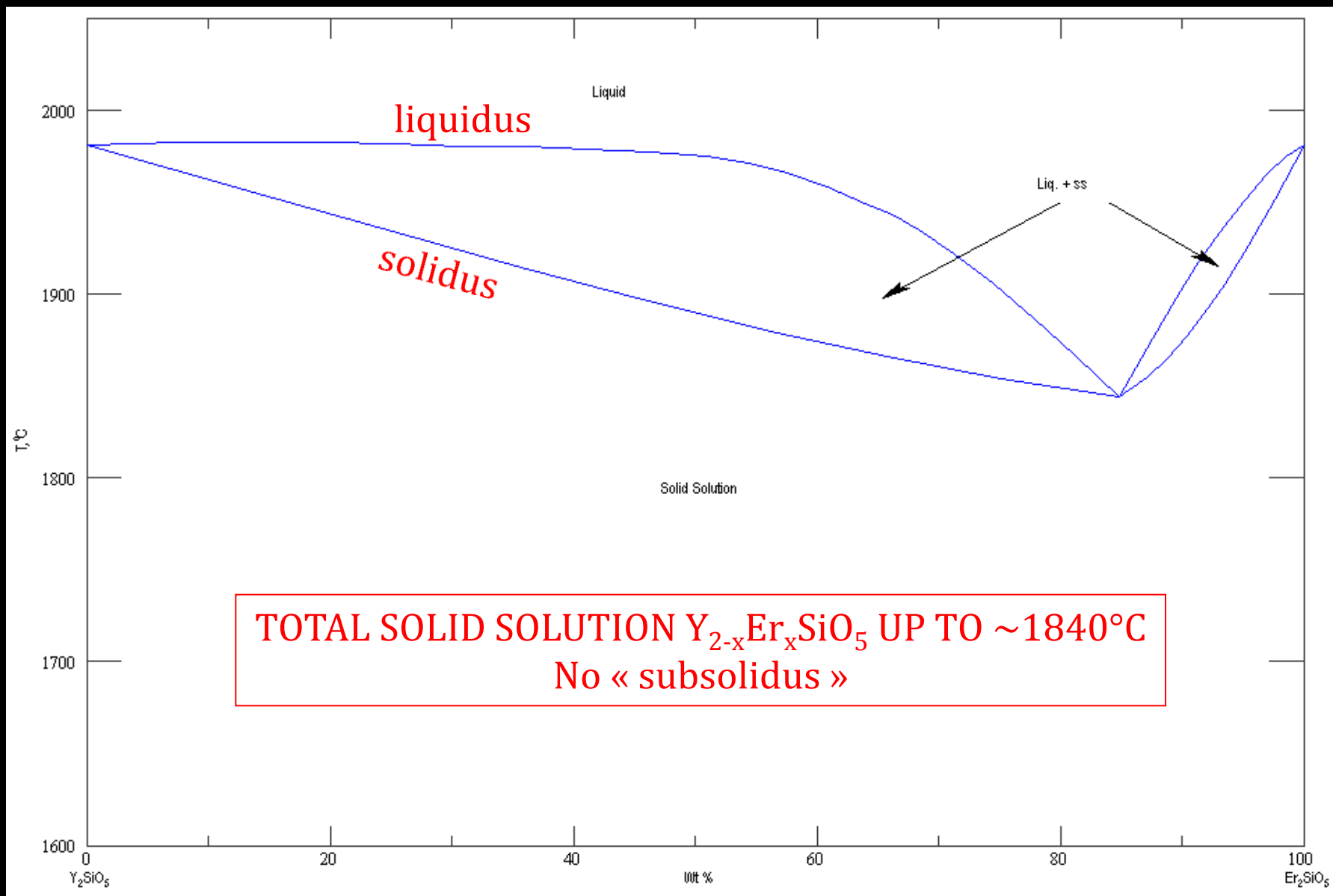
- Increasing the Er concentration in the liquid phase is all the less efficient that this amount is already large, both from the viewpoint of transfer equilibrium and that of morphological stability conditions



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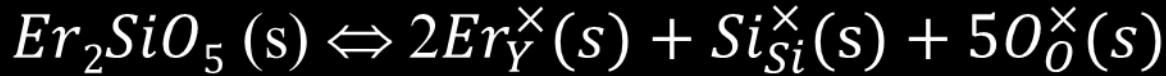
Equilibrium partition coefficient of Er^{3+} in a Y_2SiO_5 crystal grown from the melt



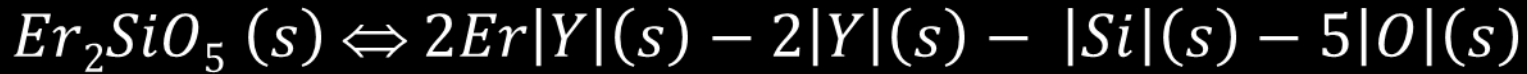
N. A. Toropov, F. Ya. Galakhov, and S. F. Konovalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 738-743 (1962); *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, No. 5, 689-693 (1962).

Equilibrium partition coefficient of Er^{3+} in a Y_2SiO_5 crystal grown from the melt (2)

If Er_2O_3 and SiO_2 react together faster than they dissolve into Y_2SiO_5



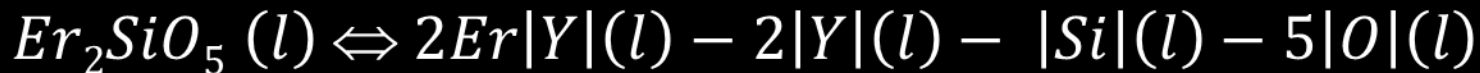
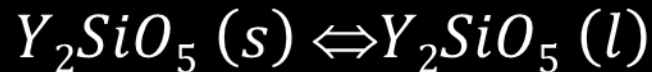
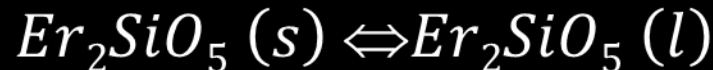
Structure elements to building units transformation and Schottky's « lattice molecule »



No mutual solubility

$$\mu_{Er|Y}^s = \frac{1}{2} (\mu_{Er_2SiO_5}^{0,s} - \mu_{Y_2SiO_5}^{0,s}) + \Delta G_{d,Er_2SiO_5}^s$$

Equilibria involving the liquid phase



Liquidus equation

$$\mu_{Er|Y}^l = \frac{1}{2} (\mu_{Er_2SiO_5}^{0,s} - \mu_{Y_2SiO_5}^{0,s} + \Delta G_{d,Er_2SiO_5}^l + \Delta G_{m,Er_2SiO_5} - \Delta G_{m,Y_2SiO_5})$$

Equilibrium condition between the solid solution and the liquid phase for every $\sim 1840^\circ C \leq T \leq T_{m,Er_2SiO_5}$: $\mu_{Er|Y}^l = \mu_{Er|Y}^s$

Equilibrium partition coefficient of Er^{3+} in a Y_2SiO_5 crystal grown from the melt (3)

$$\Delta G^s_{d,Er_2SiO_5} = \Delta G^l_{d,Er_2SiO_5} + \Delta G_{m,Er_2SiO_5} - \Delta G_{m,Y_2SiO_5}$$



$$\Delta H^s_{d,Er_2SiO_5} - T\Delta S^s_{d,Er_2SiO_5} = \Delta H^l_{d,Er_2SiO_5} - T\Delta S^l_{d,Er_2SiO_5} + \Delta G_{m,Er_2SiO_5} - \Delta G_{m,Y_2SiO_5}$$

Since $k_0 = x^s_{\text{Er}|\text{Y}} / x^l_{\text{Er}|\text{Y}}$

$$k_0 = e^{(\Delta S^s_{xc,Er|Y} - \Delta S^l_{xc,Er|Y})/R} e^{(\Delta G_{m,ESO} - \Delta G_{m,YSO} + \Delta H^l_{d,Er|Y} - \Delta U^s_{d,Er|Y} - \Delta E^s_{st,Er|Y})/RT}$$

$$\Delta H^l_{d,Er|Y} \approx \Delta U^l_{d,Er|Y}$$

$$\Delta U_d = \Delta U_B + U_{L,Er_2SiO_5} - U_{L,Y_2SiO_5}$$

$$\Delta E^s_{st,Er|Y} = 8\pi G r_Y (r_{Er} - r_Y)^2$$

$$\Delta S_{xc} = \Delta S_{ph} + \Delta S_{mag} + \Delta S_{el} + S^{0,f}_{Er_2SiO_5} - S^{0,f}_{Y_2SiO_5}, \text{ with } \Delta S_{el} \approx 0$$

Energy level diagram of a solid solution : the cases of KCl:Na⁺ and NaCl:K⁺

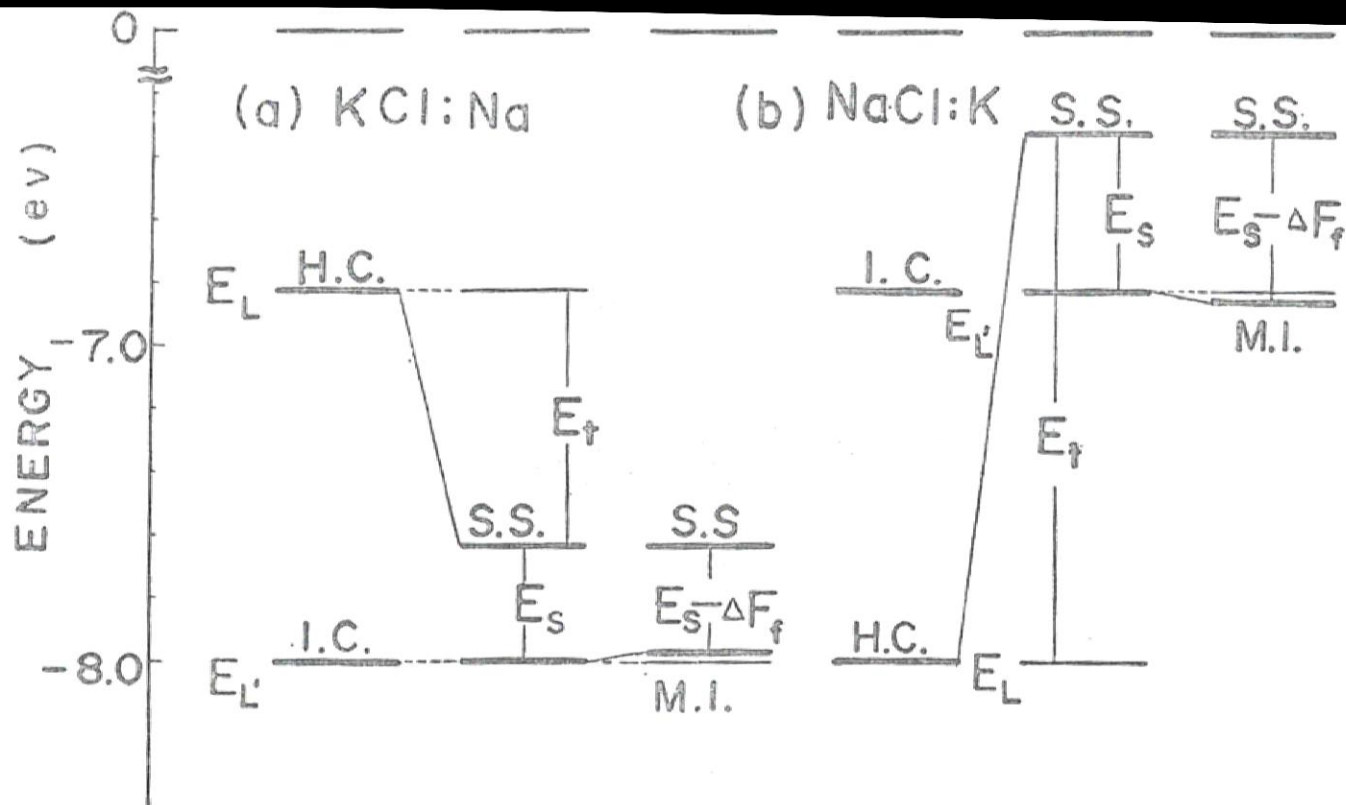


Fig. 7. The energy level diagram illustrating the energy required to introduce the impurity into the crystal from the melt.

(a) Na impurity in KCl host material

(b) K impurity in NaCl host material

The energy is expressed in eV from the vacuum level in the separated state of ions. H.C., I.C., S.S., and M.I. stand for the level of the host crystal, the impurity crystal, the solid solution, and the molten impurity crystal, respectively.

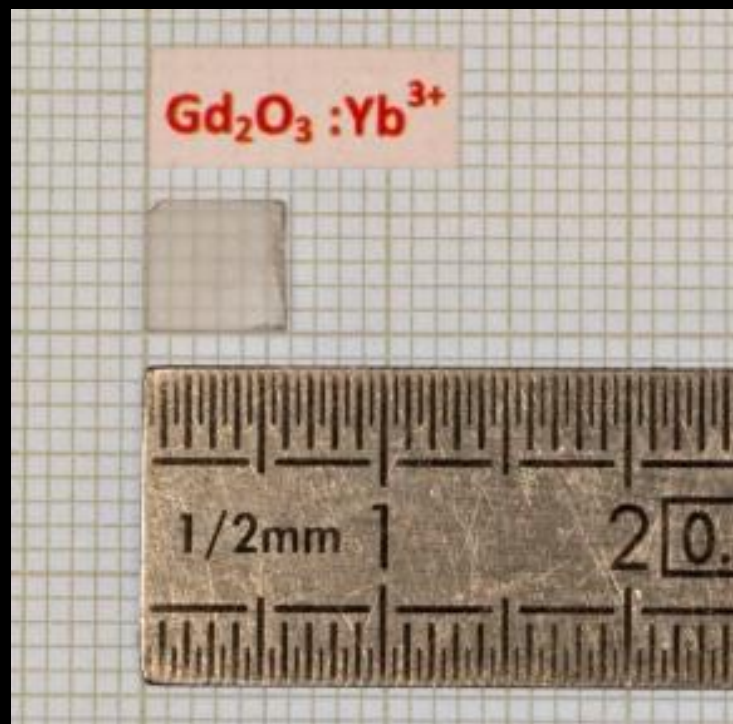
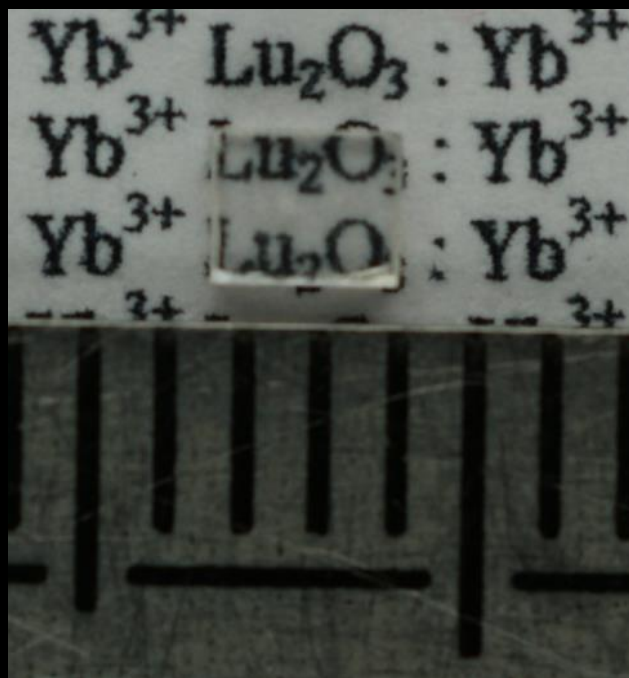
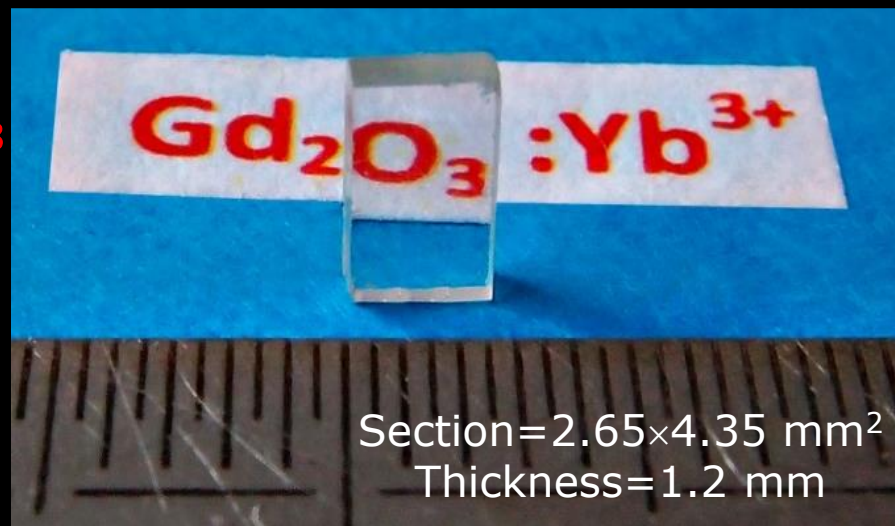
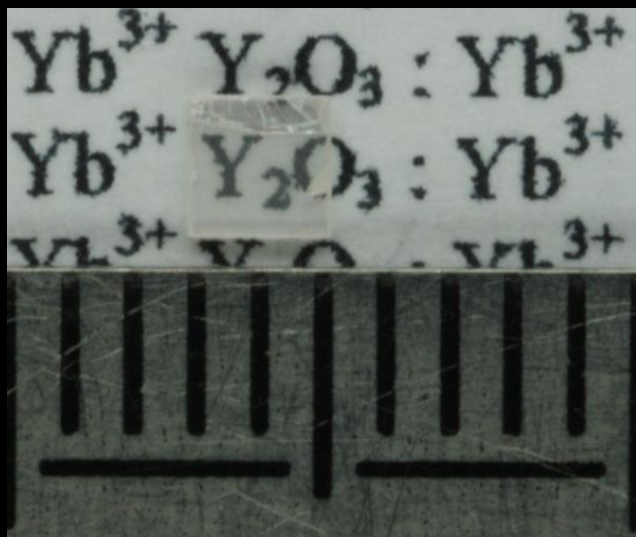
M. Ikeya *et al.*, Jap. J. Appl. Phys., 7 (8) (1968) 837-845

$$E_S \leftrightarrow \Delta U_d, E_t \leftrightarrow \Delta U_B, E_L \leftrightarrow U_L, \Delta F_f \leftrightarrow \Delta G_m$$

Outline

- Equilibrium solubility limit :
 - *Nd³⁺-doped CaWO₄*
 - *Co-doping and association to increase the solubility limit*
 - *Point defects association kinetics in Er³⁺-doped KPb₂Cl₅*
- Equilibrium partition coefficient of Er³⁺ in a Y₂SiO₅ crystal grown from the melt
- **Equilibrium partition coefficient of Yb³⁺ in a Gd₂O₃ crystal grown from a Li₆Gd(BO₃)₃ flux**
- Dopant concentration profiles in crystals grown from the melt
- Morphological instability of the solidification interface during a crystal growth experiment

Rare Earth SesquiOxides siNgle-crystAl growTh by the flux mEthod



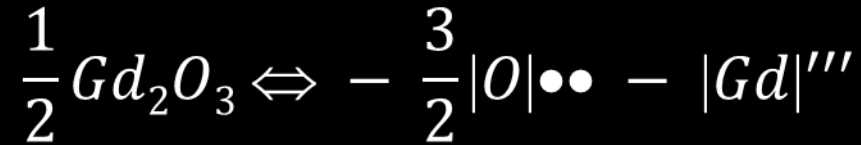
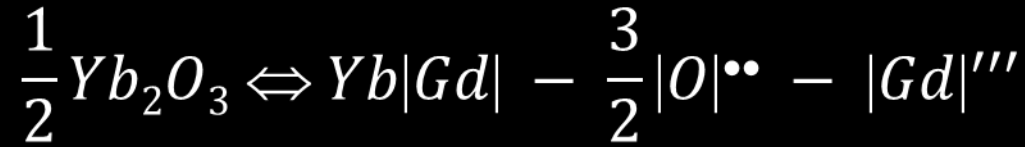
Equilibrium partition coefficient of Yb^{3+} in a Gd_2O_3 crystal grown from a $\text{Li}_6\text{Gd}(\text{BO}_3)_3$ flux

$$x_{\text{Yb}|\text{RE}}^s \approx e^{\Delta S_{v,\text{Yb}|\text{RE}}^s/2R} e^{[-\Delta U_{B,\text{Yb}|\text{RE}} - \Delta U_L - 8\pi G r_{\text{RE}}(r_{\text{Yb}} - r_{\text{RE}})^2]/2RT}$$

Yb^{3+} solubility in solid state Gd_2O_3 *a priori* much smaller than in Lu_2O_3 (at RT)

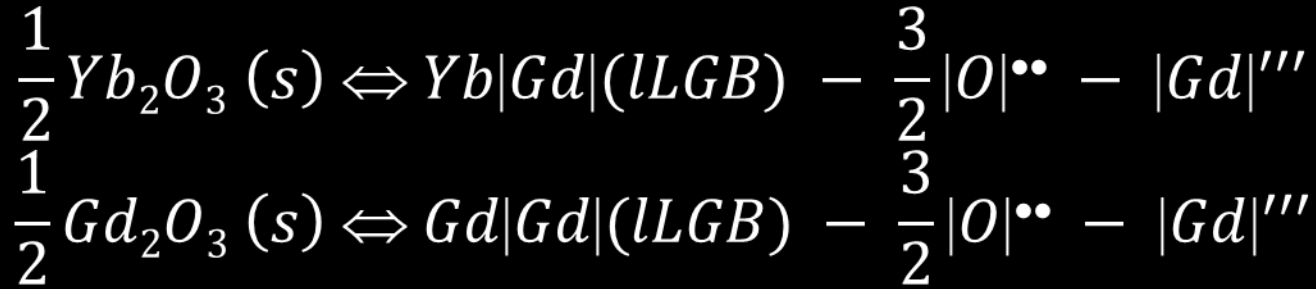
RE_2O_3	$\Delta\mu^{0,s}$ (kJ/mol)	$-\Delta U_L$ (kJ/mol)	$-\Delta E_{\text{st}}$ (kJ/mol)	$\Delta S^{0,f}$ (2R)
Gd_2O_3	+18	-413	-4.36	-1.05
Lu_2O_3	+57	-80.5	-0.07	+1.39
Y_2O_3	+81	-592	-1.16	+2.05

Equilibrium partition coefficient of Yb^{3+} in a Gd_2O_3 crystal grown from a $\text{Li}_6\text{Gd}(\text{BO}_3)_3$ flux (2)

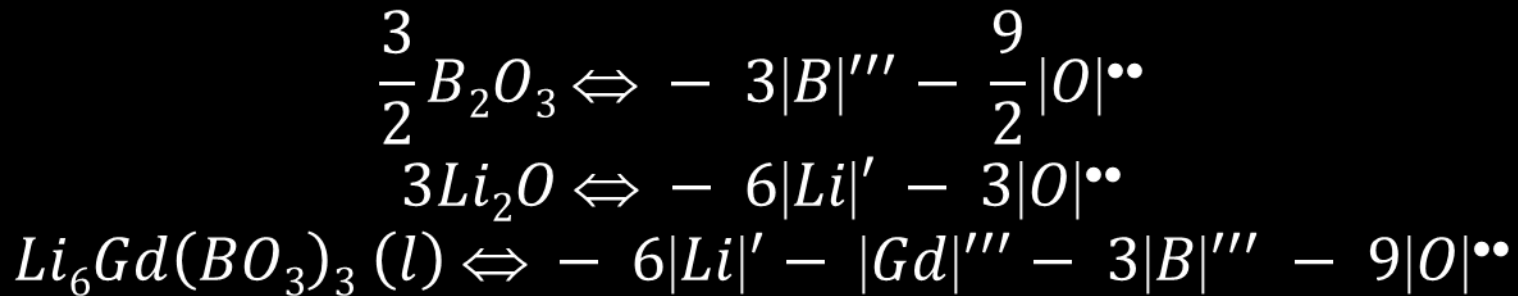


$$\mu_{\text{Yb|Gd|}}^s = \frac{1}{2} \left(\mu_{\text{Yb}_2\text{O}_3}^{0,s} - \mu_{\text{Gd}_2\text{O}_3}^{0,s} + \Delta G_{d,\text{Yb|Gd|}}^s \right) \quad (\text{A})$$

Dissolution equilibrium of Yb_2O_3 and Gd_2O_3 into liquid $\text{Li}_6\text{Gd}(\text{BO}_3)_3$:



Site conservation rule and Schottky's « lattice molecule »



$$\mu_{\text{Yb|Gd|}}^{l\text{LGB}} = \frac{1}{2} \Delta G_{d,\text{Yb|Gd|}}^{l\text{LGB}} + \frac{1}{2} \mu_{\text{Yb}_2\text{O}_3} + \frac{3}{2} \mu_{\text{B}_2\text{O}_3} + 3 \mu_{\text{Li}_2\text{O}} - \mu_{\text{Li}_6\text{Gd}(\text{BO}_3)_3}$$

$$\mu_{\text{Gd|Gd|}}^{l\text{LGB}} = \frac{1}{2} \Delta G_{d,\text{Gd|Gd|}}^{l\text{LGB}} + \frac{1}{2} \mu_{\text{Gd}_2\text{O}_3} + \frac{3}{2} \mu_{\text{B}_2\text{O}_3} + 3 \mu_{\text{Li}_2\text{O}} - \mu_{\text{Li}_6\text{Gd}(\text{BO}_3)_3}$$

As dissolution occurs in a molten flux, the standard state is no longer Raoult's but Henry's one :

$$\mu_{\text{Yb}_2\text{O}_3}^{0,s} = \mu_{\text{Yb}_2\text{O}_3}^{*,l} + RT \ln(\gamma_{\text{Yb}_2\text{O}_3}^{l,sat} x_{\text{Yb}_2\text{O}_3}^{l,sat})$$

Pure Yb_2O_3 in equilibrium with the saturated LGB solution

$$\mu_{\text{Yb}|Gd}^{LLGB} \approx \frac{1}{2} \Delta G_{\text{Yb}|Gd}^{LLGB} + \frac{1}{2} \mu_{\text{Yb}_2\text{O}_3}^{*,l} + \frac{3}{2} \mu_{\text{B}_2\text{O}_3}^{*,l} + 3 \mu_{\text{Li}_2\text{O}}^{*,l} - \mu_{\text{Li}_6\text{Gd}(\text{BO}_3)_3} \quad (\text{B})$$

$$\mu_{\text{Gd}|Gd}^{LLGB} \approx \frac{1}{2} \Delta G_{\text{Gd}|Gd}^{LLGB} + \frac{1}{2} \mu_{\text{Gd}_2\text{O}_3}^{*,l} + \frac{3}{2} \mu_{\text{B}_2\text{O}_3}^{*,l} + 3 \mu_{\text{Li}_2\text{O}}^{*,l} - \mu_{\text{Li}_6\text{Gd}(\text{BO}_3)_3} \quad (\text{C})$$

In equilibria : $\mu_{\text{Yb}|Gd}^s + \mu_{\text{Gd}|Gd}^{LLGB} = \mu_{\text{Yb}|Gd}^{LLGB}$ F. Rosenberger and H. G. Riveros
J. Chem. Phys., 60 (2) (1974) 668-673



$$\Delta G_{d,\text{Yb}|Gd}^s + \Delta G_{d,\text{Gd}|Gd}^{LLGB} + RT \ln(\gamma_{\text{Gd}_2\text{O}_3}^{LGB,sat} x_{\text{Gd}_2\text{O}_3}^{LGB,sat}) = \Delta G_{d,\text{Yb}|Gd}^{LLGB} + RT \ln(\gamma_{\text{Yb}_2\text{O}_3}^{LGB,sat} x_{\text{Yb}_2\text{O}_3}^{LGB,sat})$$

Since $k_0 \approx x_{\text{Yb}|\text{Gd}}^s / x_{\text{Yb}|\text{Gd}}^l \times x_{\text{Gd}|\text{Gd}}^l$ ($x_{\text{Gd}|\text{Gd}}^s = 1$, see eq. (A))

F. Rosenberger and H. G. Riveros
 J. Chem. Phys., 60 (2) (1974) 668-673

$$k_0 \approx \frac{\gamma_{\text{Gd}_2\text{O}_3}^{\text{LGB,sat}} x_{\text{Gd}_2\text{O}_3}^{\text{LGB,sat}}}{\gamma_{\text{Yb}_2\text{O}_3}^{\text{LGB,sat}} x_{\text{Yb}_2\text{O}_3}^{\text{LGB,sat}}} e^{\frac{[\Delta S_{v,\text{Yb}}^s + \Delta S_{v,\text{Gd}}^{\text{LGB}} - \Delta S_{v,\text{Yb}}^{\text{LGB}}]}{R}} e^{\frac{[\Delta H_{d,\text{Yb}_2\text{O}_3}^{\text{LGB}} - \Delta H_{d,\text{Gd}_2\text{O}_3}^{\text{LGB}} - \Delta U_{\text{lat}} - 8\pi G r_{\text{Gd}} (r_{\text{Yb}} - r_{\text{Gd}})^2]}{RT}}$$

Yb^{3+} partition coefficient at the Gd_2O_3 crystallization interface in the flux

Molten LGB favours the dissolution of RE impurities in Gd_2O_3 , probably
 because $x_{\text{Gd}_2\text{O}_3}^{\text{LGB,sat}} > x_{\text{RE}_2\text{O}_3}^{\text{LGB,sat}}$

Outline

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Dopant concentration profiles in normal freezing grown crystals

Van Laar (1936)

Nernst partition law

$$k_0 = \frac{x_i^S}{x_i^L} \approx \exp \left[\frac{\Delta H_f^i}{R} \left(\frac{1}{T_f^i} - \frac{1}{T} \right) \right]$$

$k_0 < 1$: direct impurity, $m < 0$

$k_0 > 1$: undirect impurity, $m > 0$

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

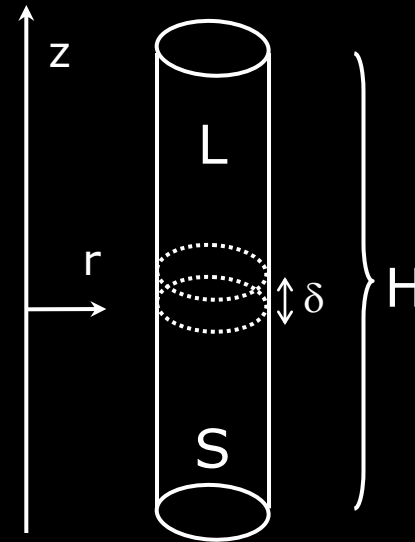
L. O. Wilson, J. Cryst. Growth, 44 (1978) 247-250/371-376

Convecto-diffusive parameter

$$\Delta = \frac{\delta v_c}{D_L}$$

J. J. Favier, Acta Metal., 29 (1981) 197-204/205-214

- equal liquid and solid densities
- diluted solutions



Dopant concentration profiles in normal freezing grown crystals (2)

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \frac{\delta v_c}{D_L}$$

- equal liquid and solid densities
- diluted solutions
- semi- ∞ liquid $H_L \gg D/v_c$

$$\Delta = 1$$

Diffusive regime

$$\delta = \frac{D_L}{v_c}, k_{eff} = 1$$

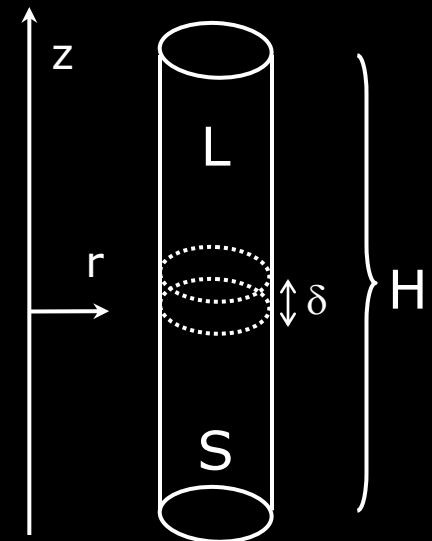
$$C(z) = C_\infty \left[1 - (1 - 2k_0) \exp\left(-\frac{k_0(1 - k_0)v_c}{D_L} z \right) \right]$$

Favier (1981)

Transient length $\propto D/(k(1-k)v_c)$

$$\Delta C(r) = \frac{C_\infty(1 - k_0)(z(0) - z(r))v_c}{D_L}$$

Coriell and Sekerka (1979)



- In a diffusive regime, axial and radial segregations cannot be decreased simultaneously by tuning only the growth rate

Dopant concentration profiles in normal freezing grown crystals (3)

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \frac{\delta v_c}{D_L}$$

- equal liquid and solid densities
- diluted solutions
- semi- ∞ liquid $H_L \gg D_L/v_c$
- "immediate" mixing in the liquid

$$\Delta = 0$$

Convective regime

$$\delta = 0, k_{eff} = k_0$$

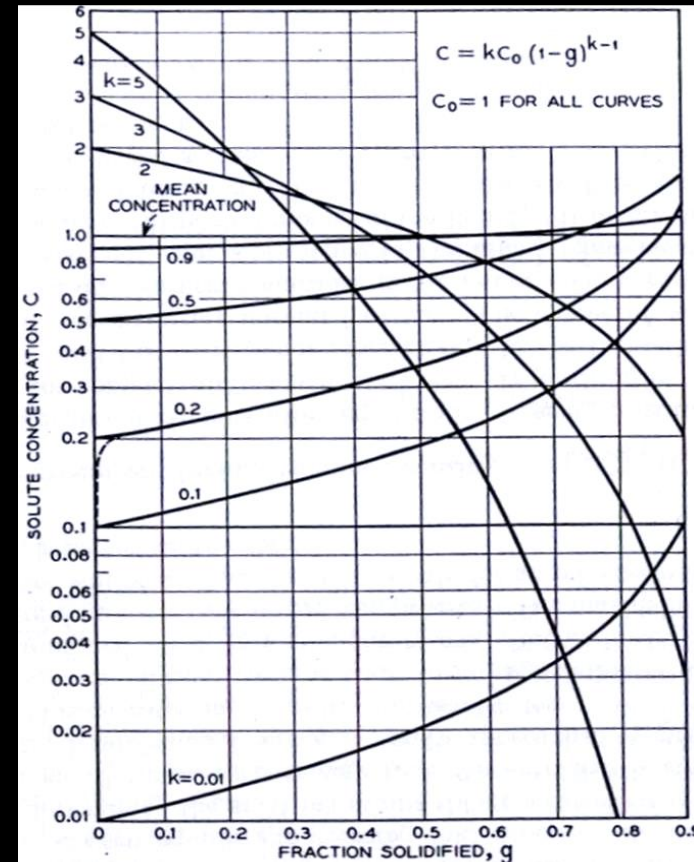
$$C(z) = k_0 C_\infty \left(1 - \frac{z}{H}\right)^{k_0 - 1}$$

Gulliver (1922)
Scheil (1942)

$$\Delta C(r) = 1.1 C_L(0) (1 - k_0) (\alpha (\delta T) g D_L^7)^{-\frac{1}{9}} v_c r^{\frac{2}{3}}$$

Kaddeche
(1996)

- In a convective regime, hydrodynamic flows decrease axial and radial segregations over a distance $\sim 0.7H$



Dopant concentration profiles in normal freezing grown crystals (4)

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \frac{\delta v_c}{D_L}$$

- equal liquid and solid densities
- diluted solutions
- semi- ∞ liquid $H_L \gg D_L/v_c$

$$0 < \Delta < 1$$

Convecto-diffusive regime

Burton, Prim
et Slichter (1953)

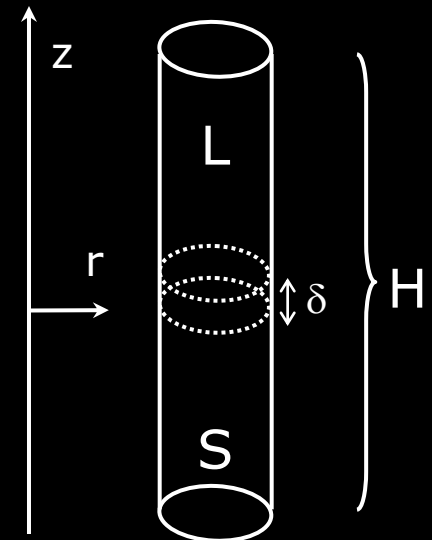
$$k_0 < k_{eff} = \frac{k_0}{k_0 + (1 - k_0)\exp(-\Delta_{BPS})} < 1, \delta_{BPS} \sim 10 - 500 \mu m$$

Modified
Gulliver (1922)/Scheil (1942)

$$C(z) = k_{eff} C_\infty \left(1 - \frac{z}{H}\right)^{k_{eff} - 1}$$

Kaddeche (1996)

$$\Delta C(r) = 6,4 \cdot 10^{-6} C_L(0) (1 - k_0) \frac{\rho \alpha (\delta T) g}{\mu D_L^2} v_c r^4$$



Experimentally, $C_S(z)/C_\infty$ can be measured at 3 different growth rates and fitted to the modified Scheil/Gulliver law to obtain k_{eff} , and then determine k_0 , δ and D_L

Dopant concentration profiles in normal freezing grown crystals (5)

The previous profiles assume that diffusion processes in the liquid and in the solid phase are limiting : they are thus kinetically controlled.

When the diffusion coefficients are high, for instance $D_s \gg rv_c$ and $D_L \gg \delta v_c$, the equilibrium is reached fastly enough so that the axial concentration profile is given by the equilibrium phase diagram and the chemical lever rule :

$$C\left(\frac{z}{H}\right) = \frac{C_\infty k_0}{a - \frac{z}{H} (a - k_0)}$$

with $a=1$ when Henry's approximation is valid. Experimentally, $C(z/H)/C_\infty$ is measured at $z \rightarrow 0$, when a seed is used, or $C(z/H)$ is fitted to this law for z/H values lower than 0.4, to obtain both C_∞ and k_0 , when nucleation occurs and traps part of the solute. H is the total length of the crystal.

Dopant concentration profiles in zone leveling grown crystals

Effective partition coefficient

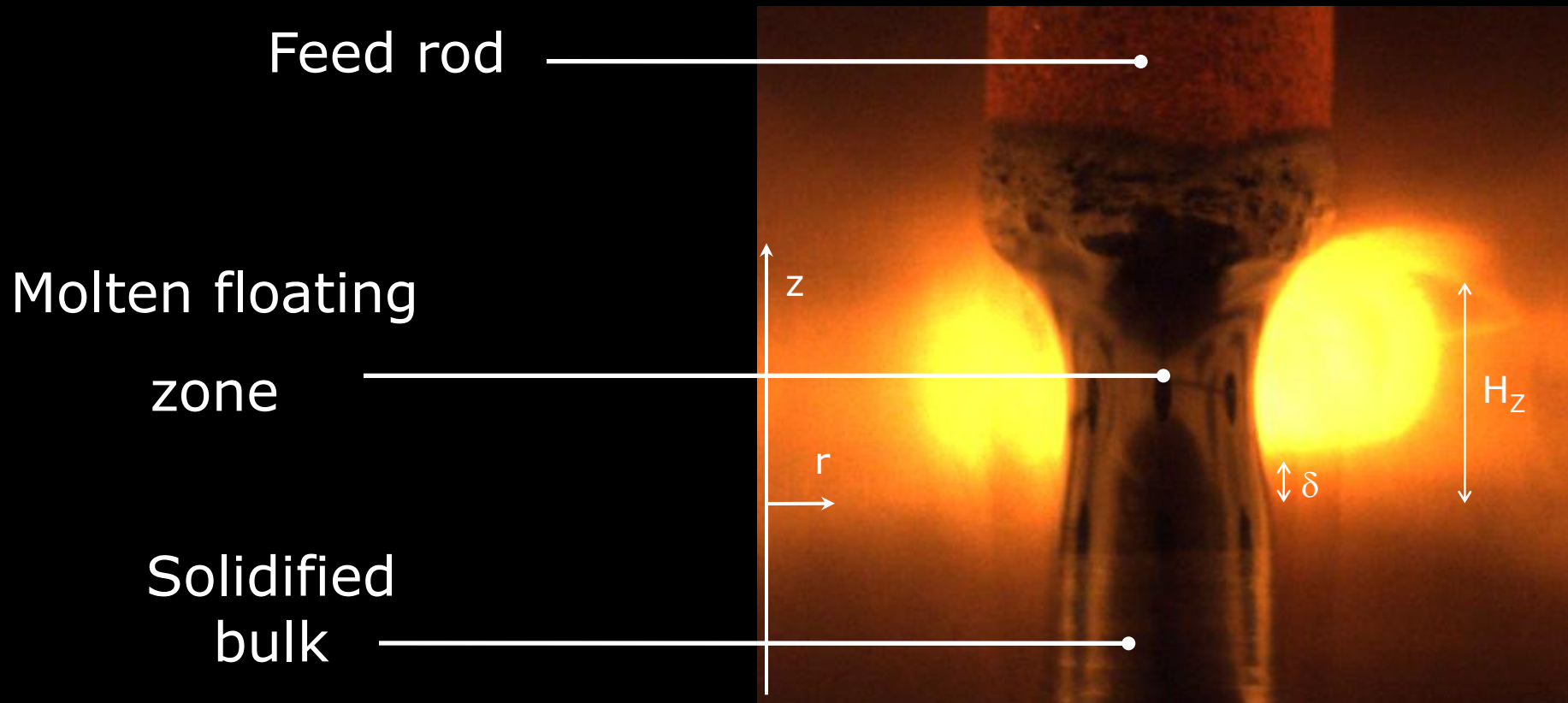
$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \min(\delta, H_z) \frac{v_c}{D_L}$$

- equal liquid and solid densities
- diluted solutions



The molten zone obtained at the focus of the optical image furnace
The feed rod diameter is 6.5 mm

Dopant concentration profiles in zone leveling grown crystals (2)

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \min(\delta, H_Z) \frac{v_c}{D_L}$$

- equal liquid and solid densities
- diluted solutions

$$\Delta \gg 5$$

Diffusive regime

Tiller « 2 » (1953)

$$C(z) = C_0 \left[1 - (1 - k_0) \exp \left(- \frac{k_0 v_c}{D_L \left(1 - \exp \left(- \frac{H_Z v_c}{D_L} \right) \right)} z \right) \right]$$

Favier (1981)

$$C(z) = C(z \geq h) + [1 - C(z \geq h)] \left[1 - \exp \left(- \frac{k_{eff} (z - h)}{H_Z} \right) \right]$$

with $h \approx 4D_L/\beta_i v_c$, $\beta_i = 1 + (1 - 2k_0)^2 \tan^2 \alpha_i$ and α_i the i^{th} root of $2\alpha_i \cos \alpha_i - (1 - 2k_0)\Delta \sin \alpha_i = 0$

Dopant concentration profiles in zone leveling grown crystals (3)

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \min(\delta, H_z) \frac{v_c}{D_L}$$

- equal liquid and solid densities
- diluted solutions

$$1 \langle \Delta \langle 5$$

Convecto-diffusive regime

Burton, Prim
et Slichter (1953)

$$k_0 \langle k_{eff} = \frac{k_0}{k_0 + (1 - k_0)\exp(-\Delta_{BPS})} \langle 1, \delta_{BPS} \sim 10 - 500 \mu m$$

Modified Pfann for $0 < z < H - H_z$

$$C(z) = C_0 \left[1 - (1 - k_{eff}) \exp\left(-\frac{k_{eff}}{H_z} z\right) \right]$$

For $z \geq H - H_z$

$$C(z) = C(H - H_z) \left(1 - \frac{z}{H}\right)^{k_{eff} - 1}$$

Dopant concentration profiles in zone leveling grown crystals (4)

Effective partition coefficient

$$k_{eff} = \frac{k_0}{1 - (1 - k_0)\Delta}$$

Wilson (1978)
Favier (1981)

Convecto-diffusive parameter

$$\Delta = \min(\delta, H_z) \frac{v_c}{D_L}$$

$$\Delta \ll 1$$

Convective regime

- equal liquid and solid densities
- diluted solutions
- virtually nil solute diffusion in the solid
- uniform concentration in the liquid
- constant r and H_z of the zone
- constant k_0 and C_0

Pfann (1953) for $0 < z < H - H_z$

$$C(z) = C_0 \left[1 - (1 - k_0) \exp\left(-\frac{k_0}{H_z} z\right) \right]$$

For $z \geq H - H_z$

$$C(z) = C(H - H_z) \left(1 - \frac{z}{H}\right)^{k_0 - 1}$$

Dopant concentration profiles in zone leveling grown crystals (5)

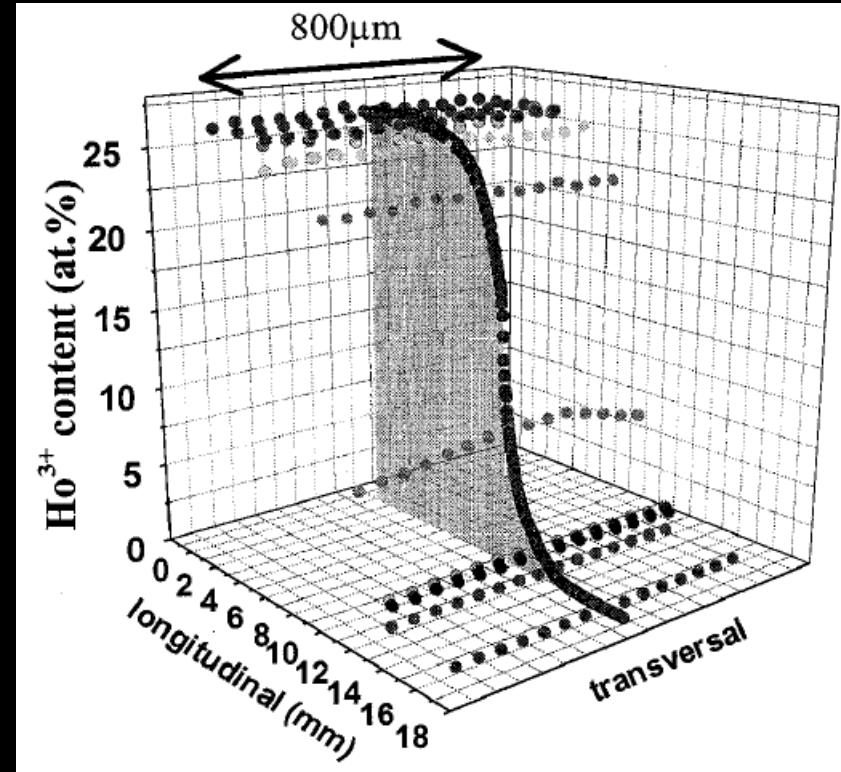
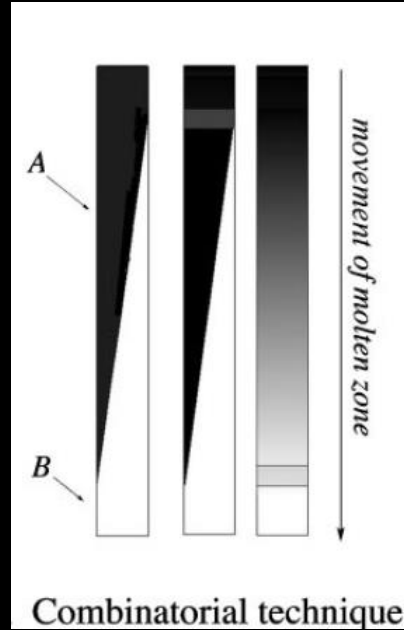
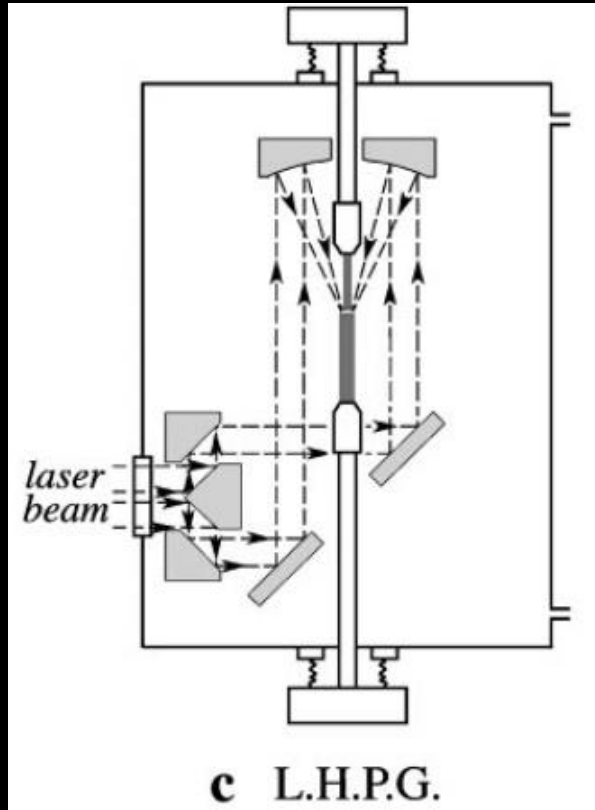
The previous profiles assume that diffusion processes in the liquid and in the solid phase are limiting : they are thus kinetically controlled.

When the diffusion coefficients are high, for instance $D_s \gg rv_c$ and $D_L \gg H_z v_c$, the equilibrium is reached fastly enough so that the axial concentration profile is given by the composition of the feed rod :

$$C\left(\frac{z}{H}\right) = C_0$$

Dopant concentration profiles in zone leveling grown crystals (6)

M. T. Cohen-Adad *et al.*, J. Phase Eq., 2001



$L \sim 15 \text{ cm} \times (50 \mu\text{m} < \phi < 1 \text{ mm})$

Composition gradient obtained in a single crystalline Y_2O_3 doped with Ho^{3+} fiber

Dopant concentration profiles in crystals grown from the melt : a tentative summary

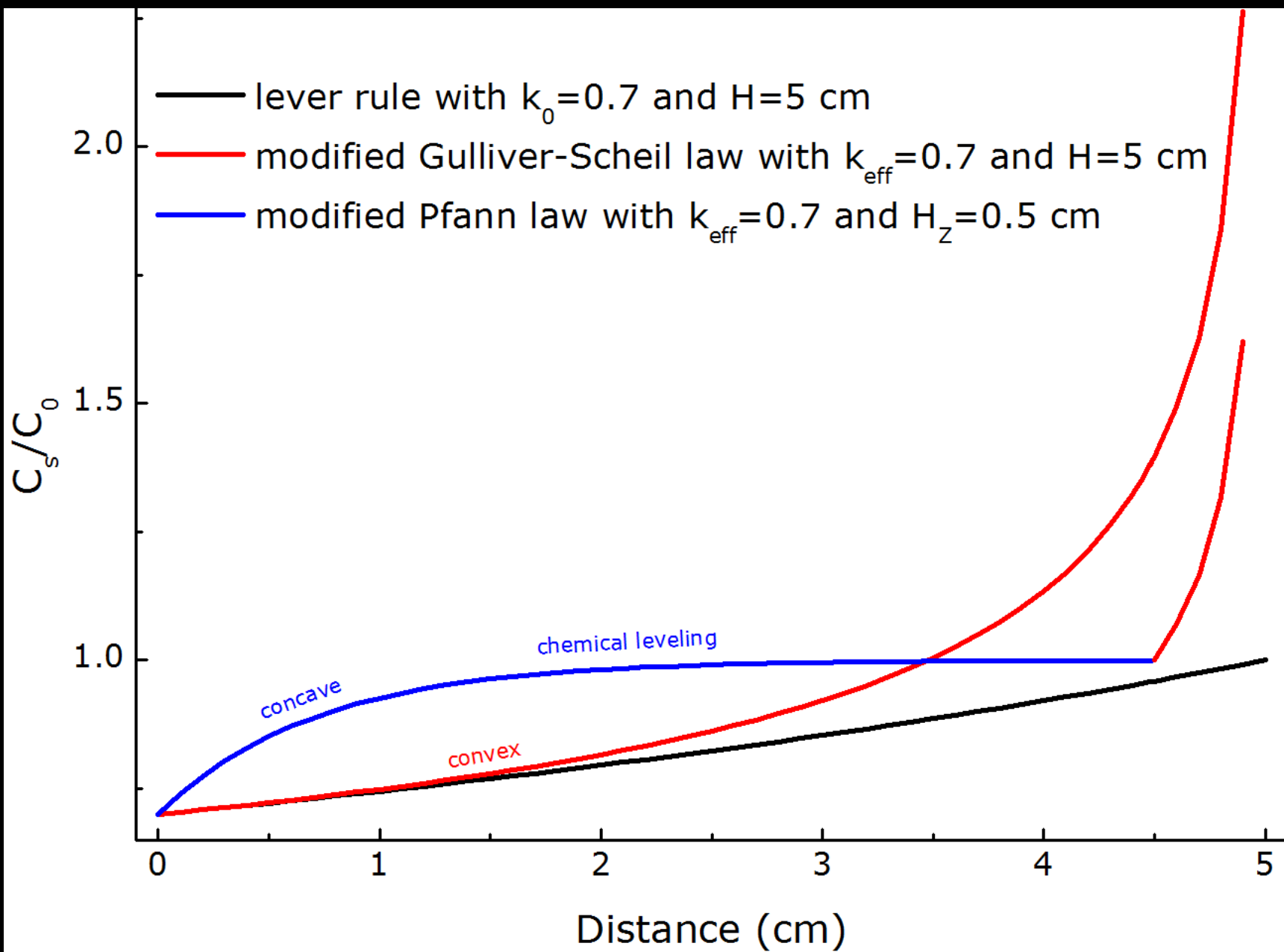
No solute feeding and semi-infinite liquid : Czochralski, Bridgman, Kyropoulos, etc.

Solute transport regime in the liquid → Solute diffusion in the liquid and in the solid phases ↓	Diffusive $\Delta = \delta v_c / D_L = 1$	Convecto-diffusive $0 < \Delta = \delta v_c / D_L < 1$	Convective $\Delta = \delta v_c / D_L = 0$
Fast	Transient : very short	Transient : very short	Transient : very short
	Stationary : lever rule	Stationary : lever rule	Stationary : lever rule
Slow $D_S \ll r v_c$ $D_L \ll \delta v_c$	Transient : Tiller « 1 » (1953), Pohl (1954), Favier (1981) (5)-ref. 2	Transient : BPS (1953), $k_0 C_0 < C_s < k_{\text{eff}} C_0$	Transient : very short
	Stationary : Tiller « 1 » (1953), Pohl (1954), Smith (1955), Favier (1981) (5)-ref. 2	Stationary : modified Gulliver-Scheil	Stationary : Gulliver (1922)-Scheil (1942)

Solute feeding and finite liquid : Verneuil, Floating zone, etc.

Solute transport regime in the liquid → Solute diffusion in the liquid and in the solid phases ↓	Diffusive $\Delta = \min(\delta, H_z) v_c / D_L > 5$	Convecto-diffusive $1 < \Delta = \min(\delta, H_z) v_c / D_L < 5$	Convective $\Delta = \min(\delta, H_z) v_c / D_L < 1$
Fast	Transient : very short	Transient : very short	Transient : very short
	Stationary : C_0	Stationary : C_0	Stationary : C_0
Slow $D_S \ll r v_c$ $D_L \ll H_z v_c$	Concave transient : Tiller « 2 » (1953), Favier (1981) (5)-ref. 2	S-shaped transient : BPS (1953), $k_0 C_0 < C_s < k_{\text{eff}} C_0$	Convex transient
	Stationary : Tiller « 2 » (1953), Favier (1981) (17)-ref. 1	Stationary : modified Pfann	Stationary : Pfann (1953)

Comparison between three widely spread concentration profiles

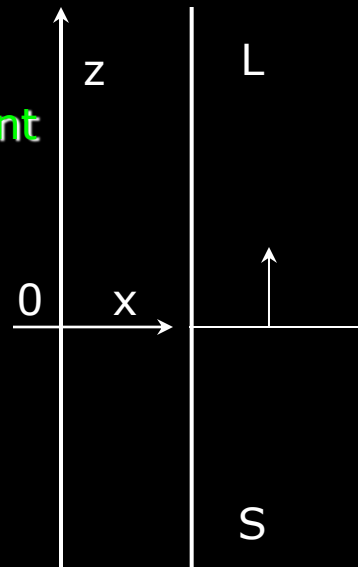


Outline

- Equilibrium solubility limit :
 - *Nd³⁺-doped CaWO₄*
 - *Co-doping and association to increase the solubility limit*
 - *Point defects association kinetics in Er³⁺-doped KPb₂Cl₅*
- Equilibrium partition coefficient of Er³⁺ in a Y₂SiO₅ crystal grown from the melt
- Equilibrium partition coefficient of Yb³⁺ in a Gd₂O₃ crystal grown from a Li₆Gd(BO₃)₃ flux
- Dopant concentration profiles in crystals grown from the melt
- **Morphological instability of the solidification interface during a crystal growth experiment**

Morphological instability by constitutional supercooling

- Non faceted growth (diffusion-controlled kinetics)
- Plane interface
- No convection
- κ , D , v_c , etc., are constant



Heat balance equation in each phase

$$\nabla^2 T_{L,S} = \frac{1}{\kappa_{L,S}} \frac{\partial T_{L,S}}{\partial t} = \frac{v_c}{\kappa_{L,S}} \frac{\partial T_{L,S}}{\partial z} \approx 0$$

Solute balance equation in the liquid phase

$$\nabla^2 C_L = -\frac{v_c}{D} \frac{\partial C_L}{\partial z}$$

Energy conservation at the liquid-solid interface

$$Lv_c = \kappa_S \frac{\partial T_S}{\partial z} - \kappa_L \frac{\partial T_L}{\partial z}$$

Solute conservation at the liquid-solid interface

$$(1 - k_0)C_L v_c = -D \frac{\partial C_L}{\partial z}$$

Continuity and thermosolutal coupling at the liquid-solid interface

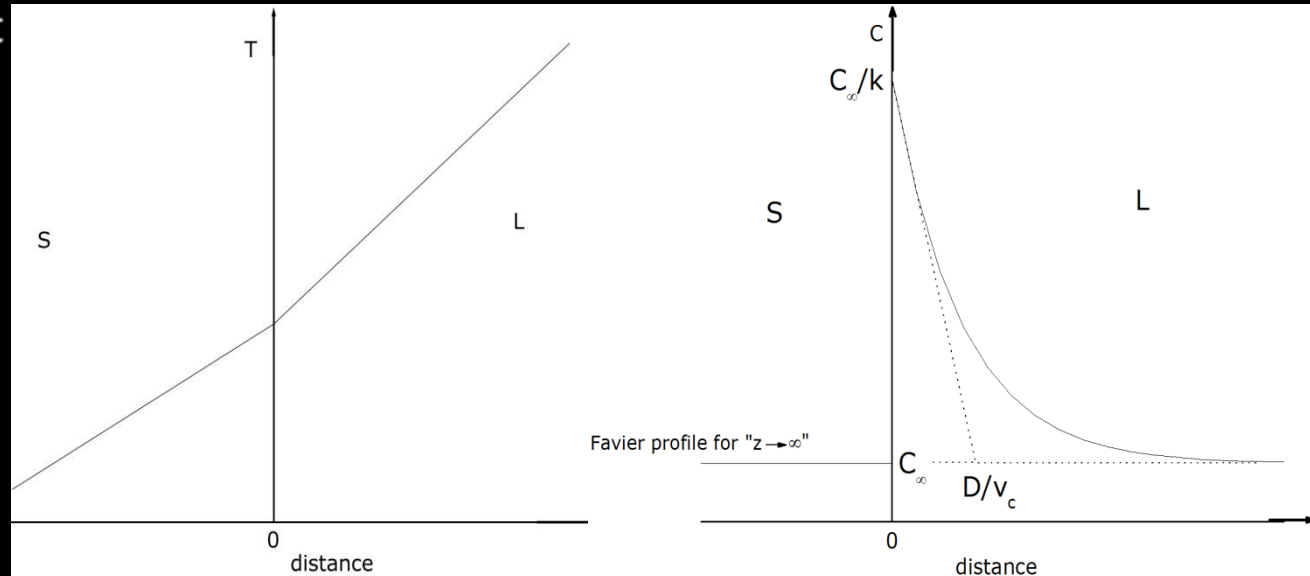
$$T_S = T_L = T_f + mC_L$$

Uniform solute concentration in the liquid phase far from the interface

$$C_L(\infty) = C_\infty$$

Morphological instability by constitutional supercooling (2)

- Non faceted growth (diffusion-controlled kinetics)
- Plane interface
- No convection
- κ , D , v_c , etc., are constant
- $k_0 < 1$, $m < 0$, are constant



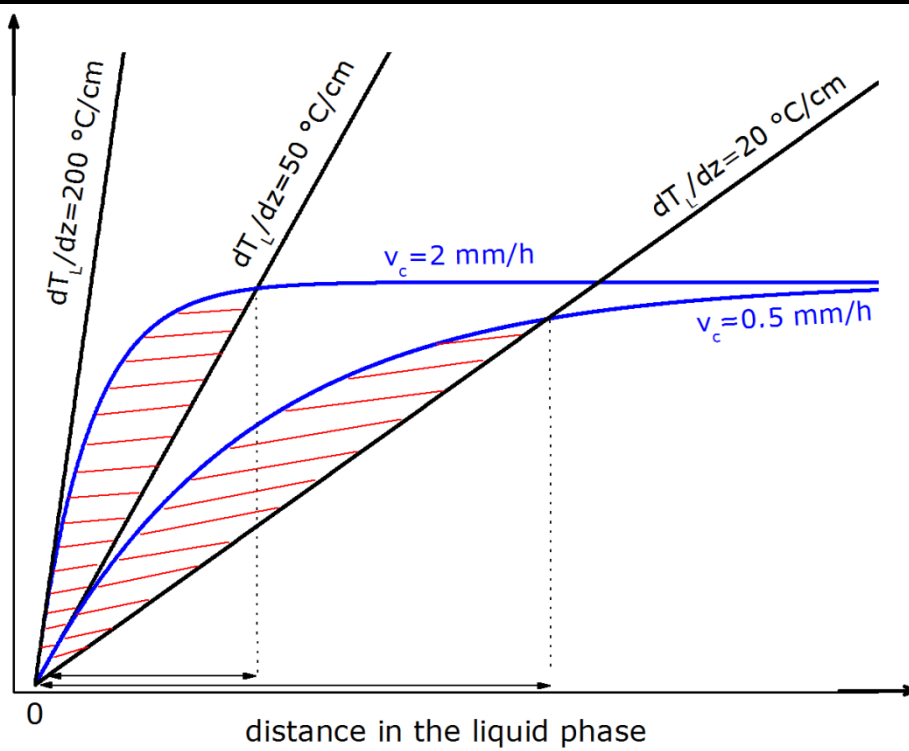
Stationary solutions found for temperature and solute distributions

$$T_S^{(0)} = T_f + m \frac{C_\infty}{k_0} + \frac{\partial T_S}{\partial z} \cdot z$$

$$C_L^{(0)} = C_\infty + C_\infty \frac{(1-k_0)}{k_0} \exp\left(-\frac{v_c z}{D}\right)$$

$$T_L^{(0)} = T_f + m \frac{C_\infty}{k_0} + \frac{\partial T_L}{\partial z} \cdot z$$

Morphological instability by constitutional supercooling (3)



a supercooled liquid zone is created above the interface over a pulling time duration corresponding to a distance (said "incubation distance") on the order of

$$-\frac{D}{k_0 v_c} \ln \left[1 - \frac{k_0 D \frac{dT_L}{dz}}{C_\infty v_c m (1 - k_0)} \right]$$

at which the instability occurs

plane



dendrites

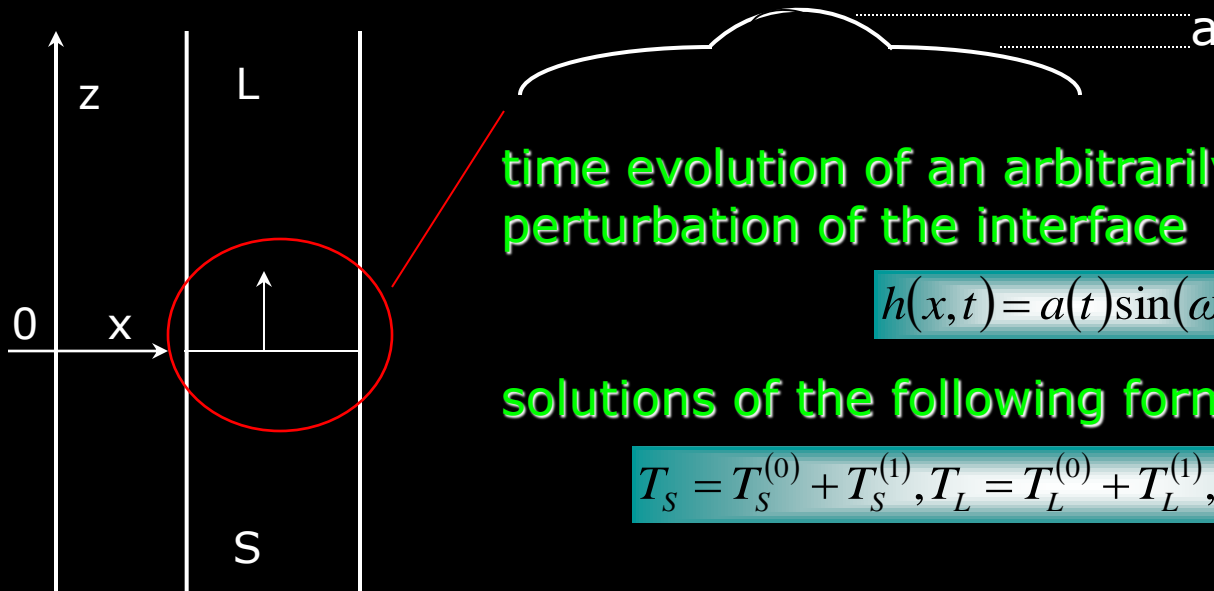
cellular

Stability criterion

$$\left. \frac{1}{v_c} \frac{dT_L}{dz} \right|_{z=0} \geq \frac{m C_\infty (1 - k_0)}{D k_0}$$

Morphological instability by constitutional supercooling (4)

- $v_c/D \ll \lambda^{-1}$
- $h \ll \lambda$



time evolution of an arbitrarily small perturbation of the interface

$$h(x, t) = a(t) \sin(\omega x)$$

solutions of the following form are looked for

$$T_S = T_S^{(0)} + T_S^{(1)}, T_L = T_L^{(0)} + T_L^{(1)}, C_L = C_L^{(0)} + C_L^{(1)}$$

Energy conservation at the liquid-solid interface

$$L \left(v_c + \frac{\partial h}{\partial t} \right) = \kappa_S \frac{\partial T_S}{\partial z} - \kappa_L \frac{\partial T_L}{\partial z}$$

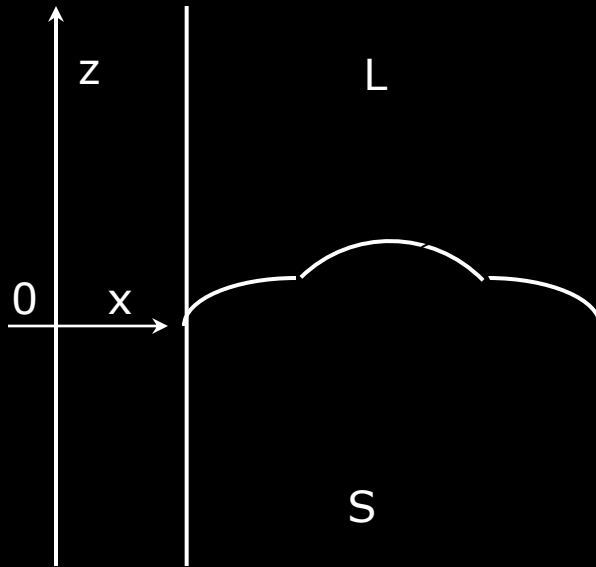
Solute conservation at the liquid-solid interface

$$(1 - k_0) C_L \left(v_c + \frac{\partial h}{\partial t} \right) = -D \frac{\partial C_L}{\partial z}$$

Continuity and thermosolutal coupling at the liquid-solid interface

$$T_S = T_L = T_f - T_f \frac{\sigma_{SL}}{L} \left(-\frac{\partial^2 h}{\partial x^2} \right) - m C_L$$

Morphological instability by constitutional supercooling (5)



In the vicinity of the instability threshold, the perturbation amplitude is

$$a(t) = a(0)e^{\frac{t}{\tau(\omega)}}$$

if $\tau(\omega) < 0$, the perturbation decays
if $\tau(\omega) > 0$, the perturbation is amplified

$$\frac{1}{\tau(\omega)} = \frac{(\kappa_S + \kappa_L)}{L} \frac{\omega \left[-T_f \omega^2 \frac{\sigma_{SL}}{L} - \langle G \rangle + mC_\infty v_c \frac{(k_0 - 1)}{Dk_0} \right]}{\left[1 + \frac{(\kappa_S + \kappa_L)mC_\infty(k_0 - 1)}{LDk_0} \right]}$$

with

$$\langle G \rangle = \frac{\kappa_S \frac{\partial T_S}{\partial z} + \kappa_L \frac{\partial T_L}{\partial z}}{\kappa_S + \kappa_L}$$

example : for pure KCl or KPb_2Cl_5 crystals

$$\tau(\omega_{\max}) \approx 0.15 \text{ s} \ll \tau_c, \tau_{\text{cool}}$$

Morphological instability by constitutional supercooling (6)

- capillarity always have a stabilizing effect
- in the absence of solute, it is necessary that $\langle G \rangle < 0$, which means $dT_L/dz < 0$ for the instability to occur for all Fourier components with $r > \lambda > 2\pi\sqrt{(T_f\sigma_{SL})/(-\langle G \rangle L)}$

for pure KCl or KPb_2Cl_5 , $\lambda_{\min} \sim 1 \mu\text{m}$

- the presence of solute always have a destabilizing effect because in this case the instability can occur for $\langle G \rangle > 0$

Mullins-Sekerka criterion

$$\frac{1}{v_c} \frac{dT_L}{dz} \geq -\frac{L}{2\kappa_L} + \frac{(\kappa_S + \kappa_L) m C_\infty}{2\kappa_L D} \frac{(k_0 - 1)}{\left(-\frac{\partial^2 h}{\partial x^2}\right)}$$

Morphological instability by constitutional supercooling (7)

- capillarity always have a stabilizing effect
- in the absence of solute, it is necessary that $\langle G \rangle < 0$, which means $dT_L/dz < 0$ for the instability to occur for all Fourier components with $r > \lambda > 2\pi\sqrt{(T_f\sigma_{SL})/(-\langle G \rangle L)}$
- the presence of solute always have a destabilizing effect because in this case the instability can occur for $\langle G \rangle > 0$

Mullins-Sekerka criterion

$$\frac{1}{v_c} \frac{dT_L}{dz} \geq -\frac{L}{2\kappa_L} + \frac{(\kappa_S + \kappa_L) m C_\infty}{2\kappa_L D} \frac{(k_0 - 1)}{\left(-\frac{\partial^2 h}{\partial x^2} \right)}$$

Experimentally, one should choose a low pulling rate and a dT_L/dz as high as possible compatible with the thermomechanical properties of the crystal

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