JOURNAL OF MATERIALS SCIENCE **28** (1993) 65–68

Electric field influence in dopant segregation in the $LiNbO_3:Cr^{3+}$ crystal growth process

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We observed, in melt crystal growth experiments, the influence of electric field on the effective segregation coefficient. An expression was developed, based on the equation of Burton, Prim and Slichter, to explain these phenomena in the crystal growth process of $LiNbO_3:Cr^{3+}$.

1. Introduction

The effective segregation coefficient is an indicator of the quantity of dopant that is incorporated in a crystal during the growth process. The most usual description of the effective segregation coefficient is based on the theory of Burton, Prim and Slichter [1] (the BPS theory), where only the normal crystal parameter dependence is considered. In some others' work [2–6] it has been observed that the effective segregation coefficient is also a function of the applied electric field in the crystal growth process. One of the reasons for which this electric field is applied in crystal growth is the possibility of obtaining single-domain ferroelectric crystals directly from the experiment without new heating for the poling process [7]. In some cases the influence of electric field in dopant incorporation is explained by a growth rate change due to the Peltier effect and constitutional supercooling [5, 6]. In another case the phenomena that explain the dopant incorporation rate changes are related to electrochemical processes in the boundary layer and ion electromigration [2–4]. All these effects normally modify the crystal growth rate due to the dopant concentration profile changes that again provoke new modifications in the dopant distribution. These studies were done by Angus *et al.* [8], Pfann and Wagner [9], Hay and Scala [10] and Verhoeven [11]. The result is an expression for the effective segregation coefficient obtained through adjustment of the BPS equation [1] given by

$$k_{\mathrm{eff}} = \left(1 + \frac{f'}{f}\right) \Big/ \left[1 + \frac{1}{k_0[1 + (f'/f)] - 1} \exp\left(-f\frac{\delta}{D}\right)\left(1 + \frac{f'}{f}\right)\right] \qquad (1)$$

where f' is the ion solute velocity due to the electric field (through the interface), f is the growth velocity, δ is the boundary layer thickness, D is the diffusion coefficient and k_0 is the equilibrium segregation coefficient. The value of f' proposed by Pfann and Wagner [9] and Verhoeven [11] is

$$f' = \mathrm{E}\Delta\mu \qquad (2)$$

where E is the applied electric field and $\Delta\mu$ is the differential ionic mobility of the solute and solvent. The value proposed by Hay and Scala [10] is

$$f = BeEZ^* \qquad (3)$$

where B is the solute mobility, e is the electronic charge, Z^* is the effective valence and E is the applied electric field. Nevertheless, these treatments, according to Hay and Scala [10], have a strong limitation for quantitative analyses due to the impossibility of accurate evaluation of f' in actual crystal growth experiments.

In this work we derived an equation that permits us to predict, quantitatively, modifications in the effective segregation coefficient due to the application of an electric field in the crystal growth process, especially applied to cases in which the electromigration of ions is predominant, and these evaluations were checked with experimental results.

2. The BPS theory modified by the action of an applied electric field

The BPS theory gives a functional variation for the effective segregation coefficient, expressed by

$$k_{\mathrm{eff}} = \frac{k_0}{k_o + (1 - k_o)\exp(-f\,\delta/D)} \qquad (4)$$

This result comes from the continuity equation

$$\partial C/\partial t = -\nabla(CV - D\nabla C) \qquad (5)$$

where V is the fluid velocity vector ($\mathrm{cm\,s^{-1}}$) and C is the dopant concentration. In order to consider the electric field influence, we must introduce a dopant ion current effect, adding a new term to the continuity Equation 5, that corresponds to the dopant ionic flux. The ionic current direction will be determined by the electric field. The new continuity equation can now be written as

$$-\nabla(CV - D\nabla C) - \frac{\partial C}{\partial t} + B\left(\nabla J_i + \frac{\partial \rho_i}{\partial t}\right) = 0 \qquad (6)$$

where J_i is the ionic current density and ρ_i the ionic charge density. The term B is a proportionality constant that supplies the necessary dimensional adjustment for the electric current continuity equation in

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BPS theory. This term will also take into consideration the polarization of the electric field in the dopant ion adsorption or desorption effect. Considering the one-dimensional problem in the stationary state, we have

$$D\frac{d^2C}{dx^2}+f\frac{dC}{dx}+B\frac{dJ_i}{dx}=0 \tag{7}$$

where J_i is the ionic current density, written in a general way as

$$J_i = N e \boldsymbol{v} \tag{8}$$

where e is the absolute value of the ionic charge, $\boldsymbol{v}$ is the velocity vector of ionic displacement and the N is the number of charge carriers per unit volume. In our case the charge carrier will be the dopant ions. We can then identify

$$\mathrm{N} = \mathrm{C} \tag{9}$$

and the proportionality constant B as

$$B = \gamma / e\boldsymbol{v} \tag{10}$$

where γ is a new proportionality constant. Under these considerations Equation 7 becomes

$$D\frac{d^2C}{dx^2}+(f+\gamma)\frac{dC}{dx}=0 \tag{11}$$

We can observe in Equation 11 that the electric field modifies the crystal growth velocity through the term γ. The new boundary conditions for this modified BPS equation will be

(a) $C = C_0$, $x = 0$ where x is measured from the crystal interface and C_0 is the interface concentration;
(b) $C = C_L$ for $x = \delta$;
(c) $(C_0 - C_S)(f+\gamma) = D(dC/Dx)$ for $x = 0$.

The solution of Equation 11 under the boundary conditions (a), (b) and (c) can be written as

$$k_{\mathrm{eff}} = \frac{k_0}{k_0 + (1-k_0)\ \exp[-(f+\gamma)\delta/D]} \tag{12}$$

where γ is the crystal growth rate modification which must be obtained as a laboratory parameter.

The simplest equation to represent γ as a function of the electric current density, we could write as follows (this case occurs when an increase in the current density causes a decrease in k_{eff})

$$\gamma = aJ \tag{13}$$

where a is a constant to be experimentally determined and J is the applied electrical current density. Combining Equations 13 and 12 we obtain

$$k_{\mathrm{eff}} = \frac{k_0}{k_0 + (1-k_0)\ \exp[-(f+aJ)\delta/D]} \tag{14}$$

For $[J] = [\mathrm{mA\,cm^{-2}}]$ and $[\gamma] = [\mathrm{cm\,s^{-1}}]$, dimensional analysis requires that $[a] = [\mathrm{cm^3\,mA^{-1}\,s^{-1}}]$. There is still the possibility (depending on the polarization of the crucible–melt system) that an increase in the current density causes a decrease in the rejection of the dopant in the solid phase, and consequently an increase in k_{eff}. We can express this variation as inversely proportional to the current density, i.e.

$$\gamma = b/J \tag{15}$$

where b is the constant to be experimentally determined. Combining Equations 12 and 15 we obtain

$$k_{\mathrm{eff}} = \frac{k_0}{k_0 + (1-k_0)\ \exp\{-[f+(b/J)]\delta/D\}} \tag{16}$$

In this case the dimensional analysis requires that $[b] = [\mathrm{mA\,cm^{-1}\,s^{-1}}]$.

3. Experimental results

In order to determine the constants a and b we must find a suitable convention for the polarization of the crucible–crystal system because, as we will observe, the value of the constant depends on the polarization, and also on the changes in the shape of the interface that are also a function of the electric field. In this paper we can use the Räuber and Feisst [3] convention that the current density is positive when the crystal is positively polarized in relation to the crucible and vice versa.

In the application of Equations 14 and 16 we consider only the module of the current density. However, when we apply an electric field positively polarized in our convention, the electrical configuration is as shown in Fig. 1a. In this case there is an electric field near the interface (from crystal to melt). Since the dopant ions are positive ($\mathrm{Cr^{3+}}$) there exists a strong tendency for dopant rejection by the effect of the electric field. These results were obtained by Räuber and Feisst [3] and experimentally confirmed in our laboratory.

When we apply an electric field in which the crystal is negatively polarized in relation to the crucible, we have a configuration as shown in Fig. 1b. There will then be a tendency to increase the dopant adsorption in the crystal.

For $\mathrm{LiNbO_3{:}Cr^{3+}}$, and current densities up to approximately 6 mA cm^{-2}, the dopant concentration starts to decrease in relation to the value predicted by the BPS theory. This behaviour is certainly related to the change in the growing interface shape. Räuber and Feisst [3] found out, for $\mathrm{LiNbO_3{:}Cr^{3+}}$, that when the current density is positive, usually a convex interface (in relation to the melt) appears, and when the current density is negative the interface is usually flat or concave. For the current density range of -6 to -15 mA cm^{-2}, however, the concentration starts to increase as one could expect.

Based on this information, we can analyse the combined effect of the interface shape and the electric field

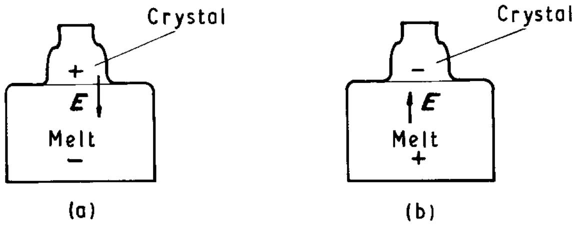

Figure 1 (a, b) Possible polarizations of the crystal–melt system.

TABLE I Polarization, interface shape, A and B constants

Polarization	Interface	Constant
$J(+)$	Convex	a_1
$J(-)$	Flat	a_2
	Concave	b_1

as shown in Table I. For a negative current density the dopant concentration change can be associated with modifications in the interface shape from convex to flat and afterwards to concave.

For the $LiNbO_3:Cr^{3+}$ data in the negative current density region we would have, in the range of approximately 0 to $6\,mA\,cm^{-2}$, a flat interface, and at approximately -6 to $-15\,mA\,cm^{-2}$ we would have a concave interface, and in the positive current density in the range of approximately 0 to $15\,mA\,cm^{-2}$ we would have a convex interface. So we must obtain experimentally three different constants to represent the effective coefficient segregation in every region. Then we could consider three distinct behaviours as described in Table I.

Using experimental results obtained by Räuber and Feisst [3] for the effective segregation coefficient of Cr^{3+} in $LiNbO_3$ (Fig. 2), where $f = 6.5\,mm\,h^{-1}$, $\omega = 34$ r.p.m. and $k_0 = 5$, it was possible to calculate the a_1, a_2 and b_1 constant values

$$a_1 = 2.48 \times 10^{-1}\,cm^3\,mA^{-1}\,s^{-1}$$
$$a_2 = 9.10 \times 10^{-2}\,cm^3\,mA^{-1}\,s^{-1}$$
$$b_1 = 3.10 \times 10^{-6}\,mA\,cm^{-1}\,s^{-1}$$

Fig. 3 shows the new behaviour of k_{eff} as a function of the electric current density in three different regions after the introduction of the correction term (Equations 16 and 14), and our experimental results.

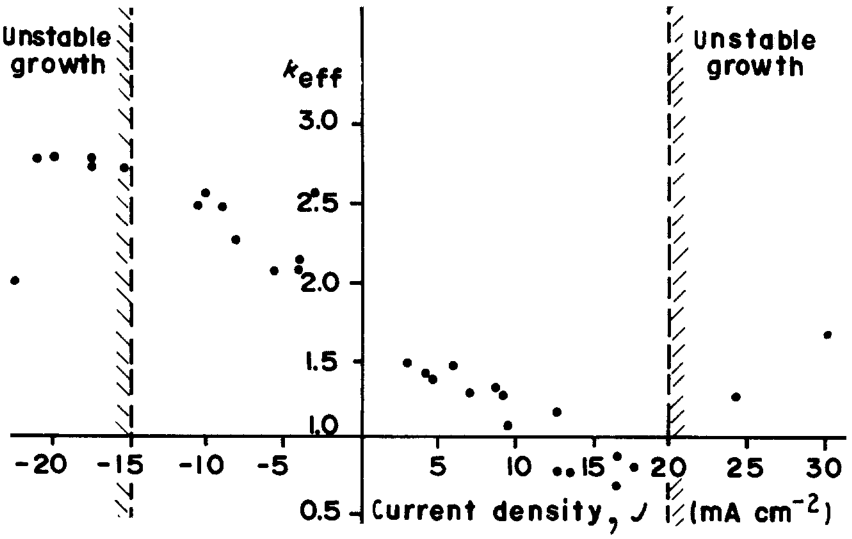

Figure 2 k_{eff} against J for $LiNbO_3:Cr^{3+}$: (●) experimental data of Räuber and Feisst [3].

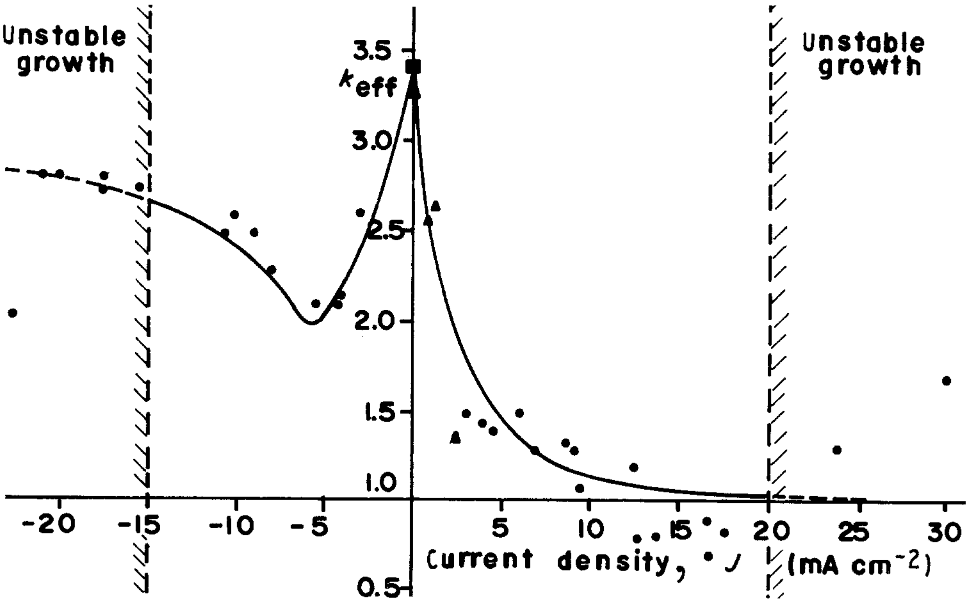

Figure 3 k_{eff} against J: (—) theoretical curve, (●) experimental data of Räuber and Feisst [3], (▲) our results, (■) value predicted by BPS theory [1]. The a_1 constant is used in the positive J region, a_2 for $-6\,mA\,cm^{-2} < J < 0\,mA\,cm^{-2}$, and b for $J < -6\,mA\,cm^{-2}$.

4. Discussion and conclusions

Through this formalization new elements are derived for the effective segregation coefficient of materials, obtained with the application of an electric field. Some of the materials do not have, obligatorily, changes in the interface due to the application of an electric field. The application of Equations 16 and 14 is general, and is subject to the same limitations as that of the BPS equation. For each material, nevertheless, there must be different values (or more than one for the same material, as for the $LiNbO_3:Cr^{3+}$ case) for the a and b constants. At the actual level of knowledge, we do not know yet whether the values of the a and b constants change with the growth parameters for the same material, or whether they change for a different kind of dopant of the same material. However, we were able to obtain values of the a and b constants through a systematic crystal growth experiment and Equations 16 and 14 were a strong tool to theoretically predict the Cr^{3+} concentration in the solid phase in new growth experiments.

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Received 13 August 1991
and accepted 7 April 1992