A mathematical model for Ti diffusion in LiNbO$_3$

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Abstract. The diffusion of titanium in crystalline lithium niobate is studied within the framework of the Nernst–Planck theory for ionic diffusion. Under this conceptualization, a concentration-dependent diffusivity emerges naturally from the mathematical model as a direct consequence of the electric field induced by ion dislocation in the lattice. Numerical simulations of the one-dimensional case show strong evidence of enhanced diffusive transport of mass. This might explain the anomalous lateral penetration of Ti in LiNbO$_3$ which has been observed in previous experiments.

1. Introduction

Optoelectronic devices for signal generation, transmission and processing are of key importance for telecommunication. The optical waveguide on planar substrate is a basic component for many integrated optical devices such as switches, modulators and filters. They can be manufactured by different processes using a large variety of materials as substrates and dopants. Basically, waveguides are made inducing spatial variation in the refractive index of some optical material. For LiNbO$_3$, *in-diffusion* of Ti is the main and well known technological process. However, some physical points of the technique still remain unclear. One controversial point concerns the diffusion path in the crystal followed by Ti through Li and/or Nb sites. According to Buchal *et al* [1] and Sugii *et al* [2], Ti *diffuses in* through Nb sites. However, Hauer *et al* [3] reported Ti diffusion into Li sites for concentrations of 1.4 mol% (2.6×10^{20} cm^{-3}). Recently on the basis of ion channelling analysis (ICA) in combination with Rutherford backscattering, particle-induced x-ray emission (PIXE) and nuclear reaction analysis (NRA), Kollewe and Kling [4] have presented a new proposal in which Ti diffuses through Li sites if the Ti concentration is below 5.9 wt%. Above this concentration, the Ti in excess of 5.9 wt% diffuses via Nb crystal sites. Another open question is the understanding of the apparent anisotropic Ti diffusion along the two directions, perpendicular and parallel to the substrate surface where the Ti source film is evaporated. Experimentally, an anomalous lateral diffusion, between two and three times the depth diffusion [4], is observed. Burns *et al* [5] as well as Fukuma and Noda [6] have explained the results by assuming an anisotropic behaviour of the diffusivity. However, the experimental results of Holmes and Smith [7] do not indicate any anisotropy for Ti diffusivity in LiNbO$_3$. They explained the enhanced lateral diffusion as a consequence of the lithium depletion in the near-surface region. Fick's second law is the classical way to model a diffusive transport phenomenon. It results in a well known partial differential equation with a constant diffusivity coefficient. Obviously, this conventional linear description of the diffusion phenomena cannot represent properly the anomalous lateral diffusion without an anisotropic diffusivity. Fontaine *et al* [8] were able

to describe the enlarged diffusion along the direction parallel to the substrate surface, solving the two-dimensional diffusive problem with a spatially dependent diffusivity along the depth direction. The origin of this spatial dependence of diffusivity is not conclusively discussed by them and has no strong physical justification. Following Kollewe and Kling [4], for titanium concentrations up to 5.9 wt%, Ti diffuses in LiNbO$_3$ replacing Nb ions in Li sites with a counter-diffusion of Nb ions, a process similar to ion exchange in glasses [9, 10]. Considering that these ions have different valences and diffusivities, we suggest that there exists an internal electric field acting simultaneously with diffusion in the global process. In this case, the Nernst–Planck conceptualization is more adequate than that originally proposed by Fick. By means of the Nernst–Planck approach for ionic diffusive transport, the main proposal of the present work is to describe the process of Ti planar *in-diffusion* through LiNbO$_3$. The results of numerical simulations will enable us to provide a satisfactory interpretation for the anomalous lateral diffusion phenomena as well as for the intrinsic nature of the mass transport process in the crystal.

2. Model formulation

In this step, we proceed with the model formulation to describe the mass transport process of Ti diffusion in LiNbO$_3$. As in the mechanism proposed by Buchal *et al* [1] and Sugii *et al* [2], we consider that Ti^{4+} diffuses in LiNbO$_3$ replacing Nb^{5+} ions. From the schematic diagram shown in figure 1, for the case in which a Ti layer covers entirely one of the crystal's surfaces, the diffusion process is considered to be one dimensional. As a first approximation, we assume that the charge balance is instantaneously achieved during the dynamics of diffusion penetration. This can be formally expressed as

$$pC_{Ti} + qC_{Nb} = C \tag{1}$$

where p and q are the valences of the Ti and Nb ions, respectively, C is an equivalent global concentration and the other variables are the concentrations of the ions identified by the subscripts. In our simulations, we consider only very low concentrations of Ti^{4+} penetrating into the crystal. As a consequence, the presence of Ti^{4+} in the bulk solid phase might be considered as a dopant ion so that we should be dealing with a typical tracer diffusion mechanism of transport. In this case, the replacement of Nb^{5+} by Ti^{4+} ions would result in a negligible overall volume change. Following the Nernst–Planck approach and making use of the simplifying assumption that the internal electric field and the gradients of Ti and Nb concentrations are collinear, the mass flux of ion i can be written as

$$J_i = -D_i \left[\frac{\partial C_i}{\partial x} + v_i \left(\frac{\mathcal{F}}{RT} \right) C_i E \right] \tag{2}$$

where D_i and v_i are the diffusivity and valence, respectively, of ion i and E is the electric field. $\mathcal{F}$ and R are the Faraday and gas constants, respectively. If no sources or sinks of charges exist, no net electric current should be present within the crystal. In this case, the following identity holds:

$$pJ_{Ti} + qJ_{Nb} = 0. \tag{3}$$

Substituting the expression for each ionic flux as given by equation (2) in equation (3), the mass flux of Ti may be written as

$$J_{Ti} = -D_{Ti} \left(\frac{\partial C_{Ti}}{\partial x} - pC_{Ti} \frac{pD_{Ti}\partial C_{Ti}/\partial x + qD_{Nb}\partial C_{Nb}/\partial x}{p^2 D_{Ti}C_{Ti} + q^2 D_{Nb}C_{Nb}} \right). \tag{4}$$

Since C is a constant, equation (1) allows one to relate the gradient of both species in the following way:

$$p\frac{\partial C_{Ti}}{\partial x} = -q\frac{\partial C_{Nb}}{\partial x}.$$

(5)

Equation (4) may then be rewritten to give

$$J_{Ti} = -D_e\frac{\partial C_{Ti}}{\partial x}$$

(6)

where D_e is an effective diffusivity given by

$$D_e = D_{Ti}\frac{C - \beta C_{Ti}}{C - \alpha C_{Ti}}$$

(7)

where $\alpha = p - (p^2/q)r$, $\beta = (p^2/q)(q - p)$ and $r = D_{Ti}/D_{Nb}$.
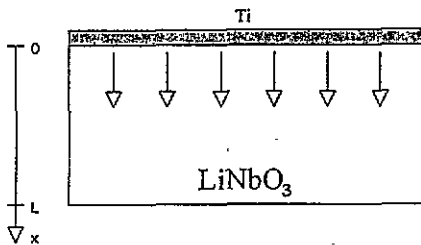

Figure 1. Schematic diagram of Ti plane *in-diffusion* into LiNbO₃.

Now, if we apply the law of conservation of mass of Ti to a fixed volume element in the crystal, one obtains, after letting the size of the control volume decrease to zero

$$\frac{\partial C_{Ti}}{\partial t} = \frac{\partial}{\partial x}\left(D_e(C_{Ti})\frac{\partial C_{Ti}}{\partial x}\right)$$

(8)

where is the non-linear partial differential equation descriptive of Ti diffusive transport into the crystal structure. The boundary and initial conditions are specially posed to represent the experimental scenario described by Holmes and Smyth [7]. At the initial time, there is no Ti present in the solid crystal and the surface layer acts as a continuous source of this element. Subsequently, at a time t_s, the surface phase will dissolve completely into the LiNbO₃ structure and all the Ti originally deposited on the film will be dispersed in the crystal phase. After that, mass is conserved in the solid and diffusion takes place to equalize gradient concentrations along the x direction. Ti will penetrate more deeply into the LiNbO₃ substrate until the concentration profile evolves to a constant value. This physical situation can be mathematically translated to the following boundary and initial conditions: the boundary conditions are

$$C_{Ti}(0, t) = \frac{C}{p} \qquad t < t_s$$

$$\left.\frac{\partial C_{Ti}}{\partial x}\right|_{x=0} = 0 \qquad t > t_s$$

(9)

$$\left.\frac{\partial C_{Ti}}{\partial x}\right|_{x=L} = 0 \qquad \forall t$$

and the initial condition is

$$C_{\mathrm{Ti}}(x, 0) = 0. \tag{10}$$

For all practical purposes, equations (8)–(10) can be expressed in dimensionless form as

$$\frac{\partial u}{\partial \tau} = \frac{1 - \beta u}{1 - \alpha u} \frac{\partial^2 u}{\partial \xi^2} + \frac{\alpha - \beta}{(1 - \alpha u)^2} \left(\frac{\partial u}{\partial \xi} \right)^2 \tag{11}$$

with, assuming that $p = 4$,

$$
\begin{aligned}
u(0, \tau) &= 0.25 & \tau &< \tau_s \\[1ex]
\left. \frac{\partial u}{\partial \xi} \right|_{\xi=0} &= 0 & \tau &> \tau_s \\[1ex]
\left. \frac{\partial u}{\partial \xi} \right|_{\xi=1} &= 0 & \forall \tau & \\[1ex]
u(\xi, 0) &= 0 &&
\end{aligned}
\tag{12}
$$

where $u = C_{\mathrm{Ti}}/C$ and we have adopted the well known parameterization for time and space: $\tau = D_{\mathrm{Ti}} t / L^2$ and $\xi = x/L$, respectively (the dimensionless switching time τ_s corresponding to $D_{\mathrm{Ti}} t_s / L^2$).

The orthogonal collocation technique [11] has been applied to solve the non-linear initial-boundary value problem given by equations (11) and (12). Firstly, equation (11) is discretized on the spatial variable ξ adopting the zeros of the Jacobi polynomials $P_N^{(0,0)}$ as normalized collocation points:

$$\frac{\mathrm{d} u_l}{\mathrm{d} \tau} = \frac{1 - \beta u_i}{1 - \alpha u_i} \sum_{j=0}^{N+1} B_{ij} u_j + \frac{\alpha - \beta}{(1 - \alpha u_i)^2} \left(\sum_{j=0}^{N+1} A_{ij} u_j \right)^2 \qquad i = 1, 2, \ldots, N \tag{13}$$

where N is the number of collocation points, and A_{ij} and B_{ij} are the orthogonal collocation coefficients for the first and second derivatives, respectively. The boundaries $\xi = 0$ and $\xi = 1$ are taken as interpolation points and the resulting system of non-linear ordinary differential equations is then integrated using a standard fourth-order Runge–Kutta method. By fixing the amount of Ti in the surface layer M_s, we can compare this quantity with the total mass dissolved in the solid phase M during the course of the process. At a given time, the Ti which has already diffused in the crystal can be readily calculated by means of the Gauss–Jacobi quadrature:

$$M = \int_0^1 C_{\mathrm{Ti}}(\xi, \tau) \, \mathrm{d} \xi \simeq \sum_{i=1}^N w_i C_{\mathrm{Ti}}(\xi_i, \tau) \tag{14}$$

where the w_i are the Gauss–Jacobi quadrature weights and the ξ_i values in the summation term correspond to the N distinct real roots of the polynomial $P_N^{(0,0)}$, all interior to the orthogonality interval $[0, 1]$. The switching time t_s refers to the moment at which the total mass of Ti present in the crystal is equal to the amount of such element originally deposited on the surface ($M = M_s$). The precision of the orthogonal collocation technique depends essentially on the number of internal collocation points, whose increase invariably leads

to a more difficult numerical integration process because of the high dimensionality and stiffness of the system of ordinary differential equations. It happens especially when sharp profiles arise and a high number of orthogonal collocation points is necessary to obtain a reasonably precise solution. The alternative approach adopted in the present work is to make use of the *finite-element collocation technique*. In this case, the collocation method is applied to subintervals of the original domain, by ensuring between them the continuity of the solution and its first derivatives. In our calculations, only two subintervals with 20 and six collocation points proved to be sufficient to generate a concentration profile with a relative precision of 10^{-4} in the worst case, when compared with lower orders of approximation.

3. Results and discussion

Our simulations have been performed for the diffusion of Ti^{4+} ($p = 4$) with the counter-diffusion of Nb^{5+} ($q = 5$). The diffusivity ratio $r = D_{Ti}/D_{Nb}$ for LiNbO₃ is a fundamental parameter required in our model which, until now, has not been obtained experimentally. Furthermore, it might vary for different sets of physicochemical conditions and different structural aspects of the crystal topology. All simulations have been performed with $L = 1$ mm. Figure 2 shows the dependence of the effective diffusivity D_e on the normalized titanium concentration C_{Ti}/C for different values of the diffusivity ratio r. For $r < 1$, the effective diffusivity is an increasing function of u in the interval $[0, 1/\alpha)$ and has a first-order pole at $u = 1/\alpha$. The dependence of D_e on C_{Ti} will be stronger, the smaller the value of the diffusivity ratio r. The linear diffusion process corresponds to $r = 1$ where the effective diffusivity becomes constant and equal to the titanium diffusion coefficient in LiNbO₃ ($D_e = D_{Ti}$). It is interesting to note that, for $r > 1$, D_e becomes a decreasing function of the titanium concentration. We classify this case as one of non-practical interest. Recent work by Carlson *et al* [12] has been devoted to demonstrating that simple driven diffusion equations with non-linearities of the type in equation (8) have a direct connection with systems in the so-called *self-organized criticality state* [13]. To be more precise, the diffusion equation with a non-linear correction such as that given by equation (7) would represent the continuous limit of certain self-organizing models. Furthermore, the singularity of such diffusivity dependence on concentration would be intimately related to a critical point for dynamical instabilities to take place. We are currently investigating these theoretical intepretations for equation (7) and more details will be given in a subsequent paper.

For comparison, simulations have been performed for three different values of the diffusivity ratio ($r = 1$, 0.5 and 0.2), all for the same set of dimensionless times. Figure 3 shows the spatial variation in titanium concentration for five distinct values of τ and a diffusivity ratio $r = 1$, corresponding to a linear process of diffusive mass transfer. As expected, an exponential-like spatial dependence is displayed at short penetration times. After the complete dissolution of the Ti covering layer at the top of the crystal surface ($\tau > \tau_s$), the concentration profile evolves gradually to a Gaussian-like shape. For even longer diffusion times, a stationary flat curve of dopant concentration will be eventually achieved in the LiNbO₃ experimental sample. From figures 4 and 5, we can clearly observe an enhanced diffusive behaviour which becomes more evident for smaller values of the diffusivity ratio, e.g. $r = 0.2$ (figure 5). This is a distinctive feature of the non-linearity described by equation (7) which can be easily quantified in terms of the switching time τ_s. The smaller the value of the diffusivity ratio r, the sooner complete penetration of the Ti surface layer will take place. This is a direct result of the intrinsic spatial and temporal
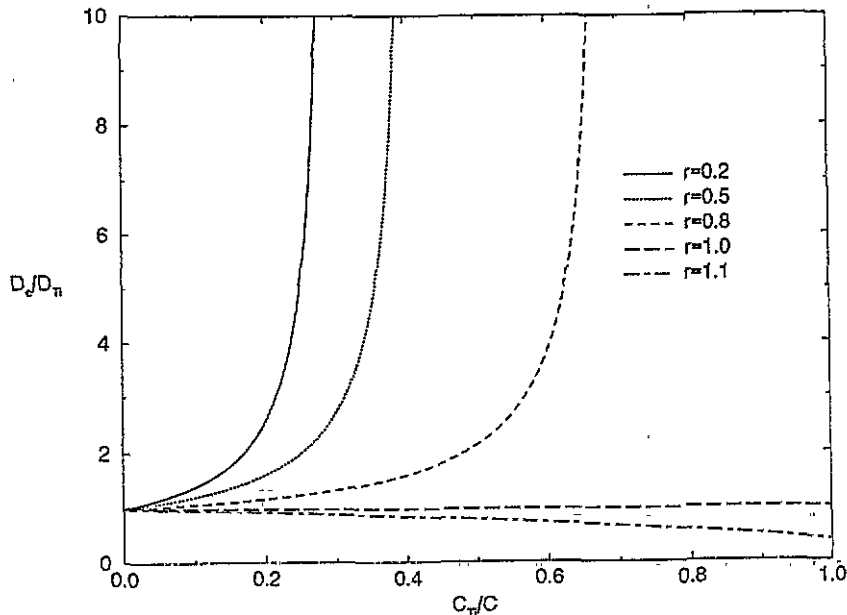
Figure 2. Effective diffusivity as a function of Ti concentration for different values of r.

variability of D_e as an explicit function of Ti concentration in the crystal. Such a tendency can be readily visualized from figures 6 and 7 where the variation in the effective diffusion coefficient with the penetration depth is shown for different values of τ and diffusivity ratios r equal to 0.5 and 0.2, respectively.

The linear description has been the most frequently utilized approach to calibrate any diffusion process. Indeed, a simple comparison between concentration profiles from linear and non-linear representations demonstrates their qualitative similarity. This resemblance would easily suggest that any single concentration profile could be simply adjusted to the linear model by means of a convenient choice of the diffusivity parameter. The inconsistency of such procedure, however, will lead to an erroneous extrapolation in time if the diffusivity is concentration dependent. In other words, the diffusion coefficient estimated for a given spatial concentration profile at a specified penetration time might not be appropriate for describing the entire dynamical evolution of the diffusion phenomena. If so, one can draw the probable conclusion that the diffusivity is concentration dependent and, as a consequence, the macroscopic description of mass transport is non-linear. As indicated by Fontaine *et al* [8], geometry may also induce significant differences between linear and non-linear representations of the diffusive behaviour. The anomalous lateral penetration observed experimentally for two-dimensional Ti diffusion in LiNbO$_3$ cannot be fully explained from a linear diffusion description except if anisotropy is invoked. This is not the case since, as already commented, the experimental results of Holmes and Smith [7] points to an isotropic diffusivity process.

4. Conclusions

A mathematical model has been devised to represent the diffusive mass transport of titanium ions in the crystalline structure of lithium niobate. The Nernst–Planck approach provided a
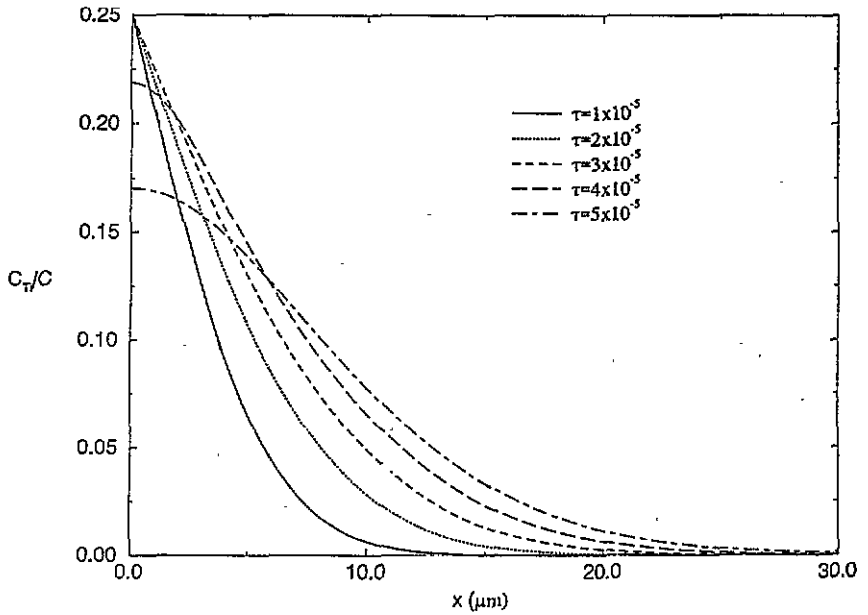
Figure 3. Spatial profiles of Ti concentration for different values of the dimensionless time and $r = 1$.
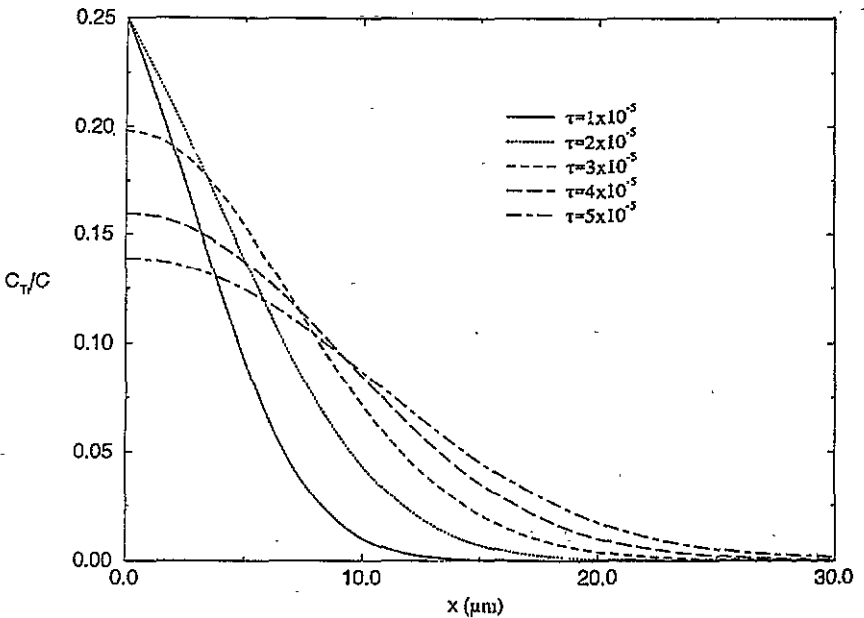

Figure 4. Spatial profiles of Ti concentration for different values of the dimensionless time and $r = 0.5$.
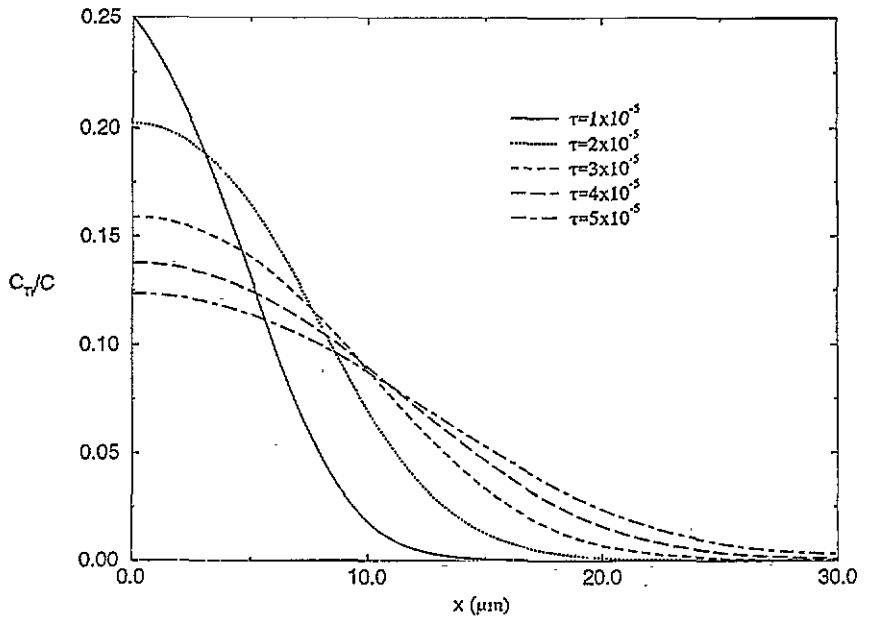
Figure 5. Spatial profiles of Ti concentration for different values of the dimensionless time and $r = 0.2$.
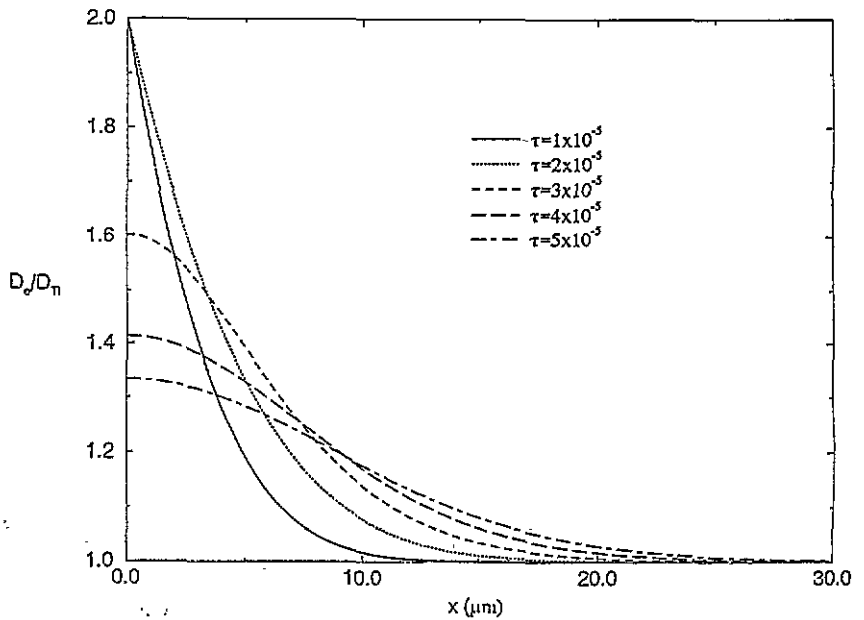

Figure 6. Spatial dependence of the effective Ti diffusivity for different values of τ and $r = 0.5$.
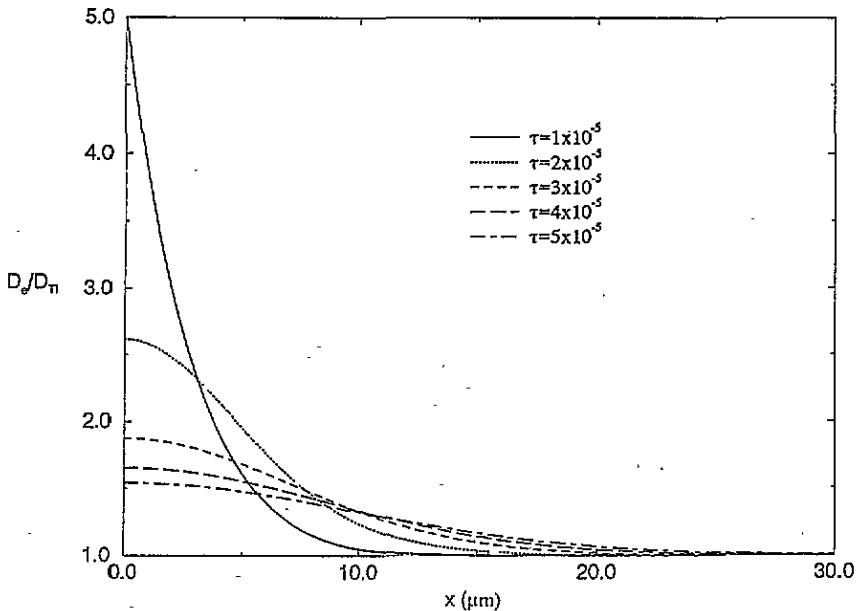
Figure 7. Spatial dependence of the effective Ti diffusivity for different values of τ and $r = 0.2$.

non-linear description of the macroscopic diffusion phenomena which might be the natural explanation for the enhanced diffusive behaviour observed in some experimental studies, *a concentration-dependent diffusivity*. The results of numerical simulations indicated how dramatic is the influence of such non-linearity on the dynamical evolution of Ti *in-diffusion* through LiNbO₃. It was shown that, for a *consistent evaluation* of the diffusivity parameter, one has to consider the *overall process* of Ti penetration into the crystal lattice. With a view to improving the performance of the system, the modelling technique developed here might be useful to assess important features of the technological process for manufacturing optical waveguides. We are currently investigating the non-linear two-dimensional case. Also, an extended version of the model will consider the diffusive transport of Ti through two different sites in parallel, namely the Li and Nb substituted positions in the LiNbO₃ crystal, according to the mechanism proposed by Hauer *et al* [3] and Kollewe and Kling [4].

Acknowledgments

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