Diffusion of Nd, Er and Nb in potassium titanyl phosphate

LETTER TO THE EDITOR

Diffusion of Nd, Er and Nb in potassium titanyl phosphate

M J Martín†, C Zaldo†¶, M F Da Silva‡, J C Soares§, F Díaz‖ and
M Aguiló‖

† Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, 28049 Madrid, Spain

‡ Instituto Tecnológico e Nuclear, Departamento de Fisica, Estrada Nacional No 10, 2685 Sacavem, Portugal

§ Centro de Fisica Nuclear da Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1699 Lisboa, Portugal

‖ Laboratori de Física Aplicada i Crista.lografia, Universitat Rovira i Virgili, 43005 Tarragona, Spain

Abstract. The concentration profiles of neodymium, erbium and niobium thermally diffused into (001) $KTiOPO_4$ single crystals have been investigated by the Rutherford backscattering spectroscopy. The activation energy E_A, and the pre-exponential factor, D_0, obtained for Nd, Er and Nb are $E_{A,Nd} = 5.3$ eV, $D_{0,Nd} = 1.3 \times 10^{-11}$ cm^2 s^{-1}; $E_{A,Er} = 6.4$ eV, $D_{0,Er} = 3.6 \times 10^{-16}$ cm^2 s^{-1} and $E_{A,Nb} = 3.8$ eV, $D_{0,Nb} = 1.2 \times 10^{-14}$ cm^2 s^{-1}.

Potassium titanyl phosphate, $KTiOPO_4$ (hereafter KTP), is one of the most attractive materials for non-linear optical and electro-optical applications because of its good non-linear optical properties and chemical stability [1].

The possible combination of the non-linear optical properties of KTP with the laser emission of Nd is hampered by the low neodymium concentration achievable in bulk crystals grown in fluxes, namely [Nd] $\approx 5 \times 10^{17}$ cm^{-3}. The incorporation of Nd_2O_3 in the flux reduces significantly the crystallization region of the KTP phase due to the nucleation of $K_3Nd(PO_4)_2$ and $NdPO_4$ phases. Moreover, the distribution coefficient of Nd in KTP is low, $K_{Nd} = 0.6 \times 10^{-3}$ [2], probably as a consequence of the large difference between the ionic radii of Nd^{3+} and Ti^{4+}. Therefore, the Nd concentration obtained in bulk crystals is much lower than the typical concentrations used in laser media, about 5×10^{20} cm^{-3}. The limitation is also found in the incorporation of other rare earth ions into KTP [3].

As an alternative method to bulk incorporation, rare earth ions may be incorporated in high concentration into the KTP surface and used in waveguide structures. Ion beam mixing has been used to incorporate Er in KTP [4], reaching doping concentrations, [Er] $\approx 2.6 \times 10^{20}$ cm^{-3}. Further, Er has been implanted and later diffused in (100) KTP by thermal annealing [5], however the diffusion process has not been quantified and an out-diffusion behaviour has been observed.

In this letter we report the thermal diffusion of Nd and Er in (001) KTP single crystals. Moreover, Nb has been diffused in order to compare the diffusion of ions with different ionic radii. The thermal diffusion coefficients in the range 750–850 °C have been determined as well as the pre-exponential factors and the activation energies.
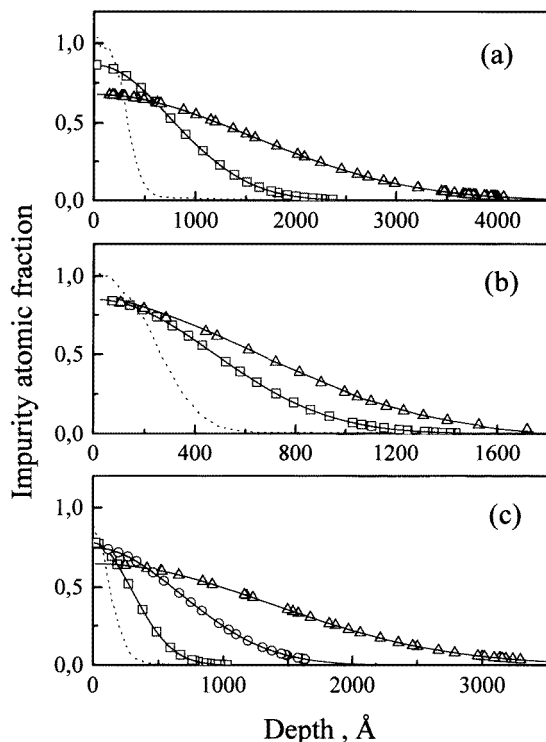
¶ Corresponding author.

Figure 1. Summary of the RBS data corresponding to the concentration profiles of the impurities for increasing times. Annealing temperature, 800 °C. The dashed lines correspond to the as-deposited states. Symbols correspond to the experimental data for increasing annealing times, t. The solid lines correspond to the fitting of the experimental data with Gaussian functions. (a) Nd: $t = 30$ min, $\square$, and 19 h, $\triangle$. (b) Er: $t = 7$ h, $\square$, and 20 h, $\triangle$. (c) Nb: $t = 30$ min, $\square$, 80 min, $\bigcirc$, and 2 h, $\triangle$.

KTP single-crystal substrates were grown by the top-seeded solution growth slow-cooling technique, using a $K_6P_4O_{13}$ flux. (001) KTP plates were oriented and polished with diamond powders.

A pulsed KrF excimer laser deposition technique was used to prepare 100 nm thick layers of Nd, Er and Nb oxides on (001) KTP single crystal. To this purpose the laser beam was focused on ceramic rotatable targets of Nd_2O_3, Er_2O_3 and Nb_2O_5 in a vacuum chamber. The laser fluence was $J = 10$ J cm^{-2}. The oxygen pressure during the deposition was 5×10^{-5} mbar and the KTP substrates were maintained at room temperature. More details about the pulsed laser deposition setup have been given elsewhere [6].

The KTP samples were placed in a Pt crucible during the thermal treatments. Diffusion was performed in the 750 to 850 °C temperature range, using a resistance furnace. Diffusion times from 10 min to 25 h were used.

The diffusion concentration profiles of Nb, Nd and Er were determined by the Rutherford backscattering spectroscopy (RBS) technique. RBS data were collected using a 3.1 Van der Graaff accelerator with 1.6 MeV He$^+$ beam collimated on the sample down to an area of 1 mm^2. Backscattered ions were simultaneously detected by two surface barrier detectors of 12 and 18 keV energy resolution, at 180 and 140° to the beam direction, respectively.

Figure 1 shows a summary of the impurity diffusion profiles obtained from the RBS
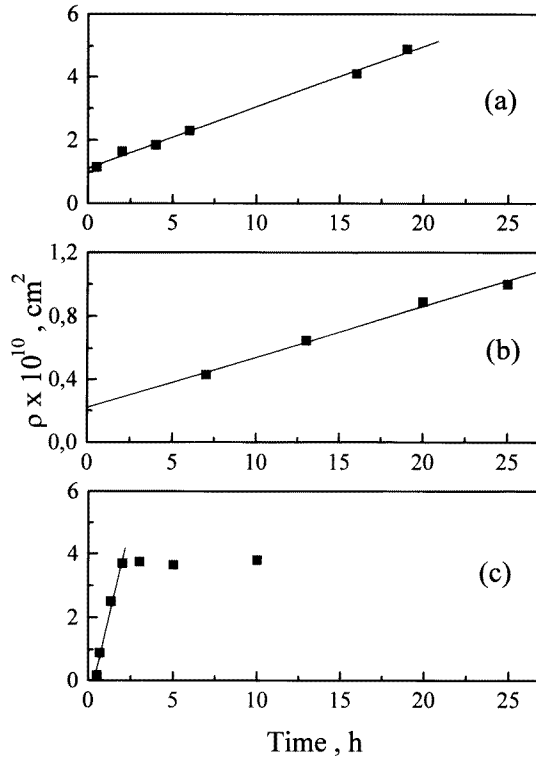
Figure 2. ρ as a function of the annealing time. The points stand for the values obtained by fitting the RBS concentration profiles and the continuous lines are the best linear fits obtained. (a) Nd (b) Er (c) Nb.

spectra in KTP samples at increasing diffusion times. The impurity concentration profile $C(x)$ was fitted by using the RUMP software [7]. The profiles have been fitted by using Gaussian functions, as expected when the diffusion time is comparable to the time required for a total diffusion of the metal in the bulk. Figure 1 also shows the fitting curves obtained.

The Gaussian impurity concentration profile, $C(x)$, is expressed as:

$$C(x) = C_0 \exp\left(-\frac{x^2}{4Dt}\right) \tag{1}$$

where x is the depth below the surface, C_0 the concentration at the surface, D the diffusion coefficient and t the diffusion time. The diffusion coefficient is related to the diffusion temperature by the well known Arrhenius equation:

$$D = D_0 \exp\left(\frac{-E_A}{kT}\right) \tag{2}$$

where D_0 is the pre-exponential factor, E_A the activation energy and k the Boltzmann constant.

Equation (1) can be re-written as a function of two parameters, C_0 and ρ, namely: $C(x) = C_0 \exp(-x^2/\rho)$, with $\rho = 4Dt$. At a given temperature, these parameters have been determined at increasing times by fitting the corresponding experimental RBS spectra. This allows us to determine the diffusion coefficients for Nd, Er and Nb.
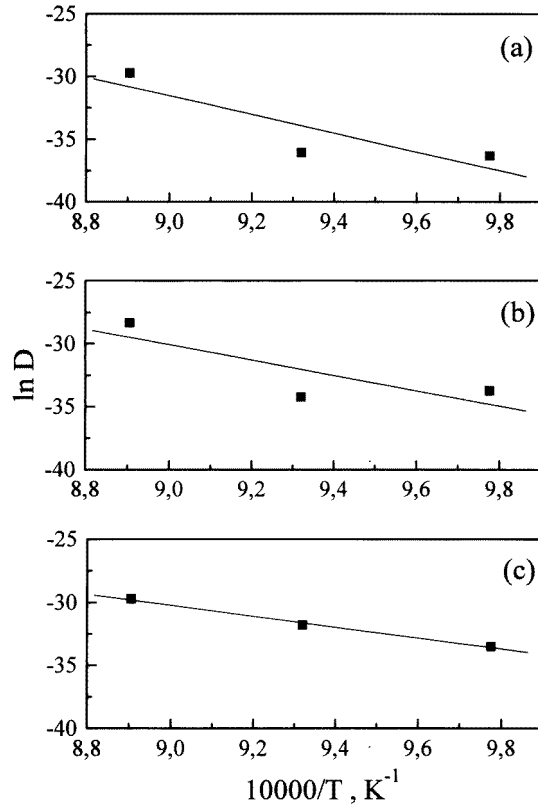
Figure 3. Arrhenius plots for Nd (a), Er (b) and Nb (c). The points are the experimental data and the continuous lines are the best linear fits obtained.

Figure 2 shows the dependence of ρ versus time at 800 °C and the linear fits performed to obtain the diffusion coefficient at this temperature. For the times considered, the ρ against t plot of Nd and Er diffused KTP shows a linear behaviour. This linear behaviour has also been observed in Nb diffused samples, but only in the shortest times considered. For diffusion times larger than 2.5 h a saturation is observed. The saturation observed in the Nb concentration could be due to the reaching of the Nb solubility limit in KTP or to the transformation of the deposited Nb oxide layer in a new compound.

The crystallinity and phases of the oxide top layer have been studied by grazing angle x-ray diffraction and in conventional θ–2θ scans, after 10 h of annealing time. We have not observed any new phase, therefore we conclude that the niobium saturation is a consequence of the solubility of Nb in KTP. We estimate the niobium limit of solubility to be about 6×10^{21} cm^{-3}.

In order to calculate the pre-exponential factor and the activation energy, additional thermal diffusion treatments at 750 and 850 °C have been performed at a fixed time. Figure 3 shows the Arrhenius plots obtained for Nd, Er and Nb. The pre-exponential factors and the activation energies calculated from the fits have been summarized in table 1.

The activation energy obtained for niobium, with the smallest ionic radius ($r_{Nb} = 0.7$ Å), is only slightly lower than those obtained for neodymium and erbium, in spite of their larger

Table 1. Pre-exponential factors, D_0, and activation energies, E_A, obtained for the diffusion of Nd, Er and Nb in (001) KTP.

	Nd	Er	Nb
D_0, cm^2 s^{-1}	1.3×10^{-11}	3.6×10^{-16}	1.2×10^{-4}
E_A, eV	5.3	6.4	3.8

ionic radii ($r_{Nd} = 1.08$ Å; $r_{Er} = 0.96$ Å). The small differences observed suggest that the physical diffusion mechanism is similar in the three cases considered. The KTP lattice has structural empty channels along the [001] lattice direction [1]. Potassium ions are located at the sides of the channels. It seems likely that the ion diffusion occurs along these channels involving potassium mobility.

The thermal diffusion coefficients calculated for Nd and Er in LiNbO$_3$ at 1027 °C are 1×10^{-13} and 0.2×10^{-13} cm^2 s^{-1}, respectively [8] and the value calculated for Ti in LiNbO$_3$ at 1050 °C is 26–10.6 $\times 10^{-13}$ cm^2 s^{-1} [9]. The diffusion coefficients obtained at 850 °C for Nd, Er and Nb are in the range 5–1 $\times 10^{-13}$ cm^2 s^{-1}. The fact that similar diffusion coefficients are obtained at a much lower temperature, shows the efficiency of the diffusion process in KTP.

In conclusion, Nd-, Er- or Nb-diffused layers have been prepared in KTP by thermal annealing. The impurity concentrations obtained are above 10^{21} cm^{-3}, being therefore high enough to demonstrate efficient optical emission of rare-earth impurities. The activation energy and pre-exponential factor of Nd, Er and Nb in (001) KTP have been determined.

References

[1] Bierlein J D and Vanherzeele H J 1989 *J. Opt. Soc. Am.* B **6** 622
[2] Zaldo C, Aguiló M, Díaz F and Loro H J 1996 *J. Phys.: Condens. Matter* **8** 10 693
[3] Solé R, Nikolov V, Koseva I, Peshev P, Ruiz X, Zaldo C, Martín M J, Aguiló M and Díaz F 1997 to be published
[4] Wang K M, Wang W, Ding P J, Lanford W A and Liu Y G 1995 *J. Appl. Phys.* **77** 3581
[5] Wang K M, Ding P J, Wang W, Lanford W A, Li Y, Li J S and Liu Y G 1994 *Appl. Phys. Lett.* **64** 3101
[6] Alfonso J E, Martín M J, Mendiola J, Ruiz A, Zaldo C, Da Silva M F and Soares J C 1996 *J. Appl. Phys.* **79** 8210
[7] Doolittle L R 1985 *Nucl. Instrum. Methods* B **9** 334
[8] Buchal Ch and Morh S 1991 *J. Mater. Res.* **6** 134
[9] Holmes R J and Smyth D M 1984 *J. Appl. Phys.* **55** 3531