



ELSEVIER

Optical Materials 13 (1999) 175–180



# Progress in crystal growth and characterisation of rare-earth doped non-linear KTP crystals for laser applications

C. Zaldo <sup>a,\*</sup>, M. Rico <sup>a</sup>, F. Díaz <sup>b</sup>, J.J. Carvajal <sup>b</sup>

<sup>a</sup> Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, 28049 Madrid, Spain

<sup>b</sup> Laboratori de Física Aplicada i Cristallografia, Universitat Rovira i Virgili, 43005 Tarragona, Spain

## Abstract

The incorporation of rare earth ions into  $\text{KTiOPO}_4$  crystals and into other isomorphous phases is more efficient for impurities of small ionic radius. Some of the  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  spectroscopic properties in  $\text{KTiOPO}_4$  (KTP) and  $\text{RbTiOPO}_4$  (RTP) are discussed to illustrate the contribution of several centres to the optical absorption and photoluminescence properties. The  $\text{Nd}^{3+}$  centres observed in  $\text{KTiOPO}_4$  crystals grown in a W-rich flux have larger optical absorption cross sections than those observed in KTP crystals grown in a self-flux. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

$\text{KTiOPO}_4$  (KTP) crystals have been widely used as second harmonic generating elements of Nd:YAG lasers [1] and in optical parametric oscillator systems [2]. At room temperature, KTP can be phase matched for second harmonic generation (SGH) up to 994 nm. The phase matching SHG cut-off wavelength can be extended to 892 nm by doping with Nb [3]. This offers the opportunity to frequency-double diode laser emissions to produce blue light.

The good non-linear optical (NLO) properties of KTP crystals and some of their isomorphous phases, mainly  $\text{RbTiOPO}_4$  (RTP), would make of these materials good candidates for self-induced non-linear phenomena, if properly doped crystals were available. Unfortunately, the growth of KTP

crystals doped with rare earth (RE) impurities has not been reported until very recently [4]. The purpose of this work is to summarise the work performed up to now in our laboratories, and to draw conclusions which may guide towards the development of doped KTP crystals useful as laser matrices.

## 2. Crystal growth and surface modifications

The crystal growth of RE-doped KTP has been pursued by the Top Seeded Solution Growth (TSSG) slow cooled technique. Details of the experimental method and fluxes used have been reported previously [4]. In addition to self-flux, W-rich flux has been used to increase the crystal growth rate. In the latter crystals, W is efficiently incorporated into the lattice.

Two facts limit the incorporation of RE ions into the KTP lattice. On the one hand, the presence of RE ions in the melted flux induces the

\*Corresponding author. Tel.: +34-91-3349-057; fax: +34-91-3720-623; e-mail: cezaldo@icmm.csic.es

nucleation of new phases, namely  $\text{REPO}_4$  and  $\text{K}_3\text{RE}(\text{PO}_4)_2$ . Moreover, the KTP nucleation region in the phase diagram becomes narrower due to shifting of the borders with the neighbouring phases (mainly  $\text{REPO}_4$  and  $\text{K}_4\text{P}_2\text{O}_7$  ones). Above a certain critical RE concentration in the starting flux, the KTP phase does not nucleate. The critical concentrations of the studied RE ions are in the 3–8 mol% range. On the other hand, the distribution coefficient of RE ions in KTP is low. Fig. 1 shows the values obtained for  $\text{RE}^{3+}$  ions as a function of the ionic radius. The most likely lattice sites for RE in the KTP lattice are the Ti-site and the K-site. The ionic radii of these host cations are  $R(\text{Ti}^{4+}) = 0.605 \text{ \AA}$  and  $R(\text{K}^+) = 1.51 \text{ \AA}$ , while the ionic radii of rare earth are in the 0.861–0.983  $\text{ \AA}$  range. The fact that the distribution coefficient of the rare earth ion decreases as its ionic radius increases suggests that  $\text{RE}^{3+}$  ions substitute the  $\text{Ti}^{4+}$  of the lattice.

These facts presently limit the RE concentration in bulk crystals to 50–600 ppm ( $\approx 5 \times 10^{17}$ – $6 \times 10^{18} \text{ cm}^{-3}$ ), which is well below the concentrations used in RE-doped laser matrices (typically in the  $10^{20}$ – $10^{21} \text{ cm}^{-3}$  range). The optical absorption associated with these low concentration levels is consequently very low, and far from that re-

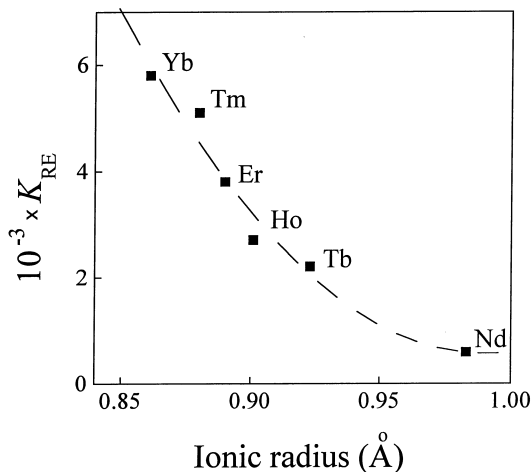


Fig. 1. Distribution coefficient ( $K_{\text{RE}} = (\text{RE}/(\text{RE} + \text{KTP}))_{\text{crystal}} / (\text{RE}/(\text{RE} + \text{KTP}))_{\text{melt}}$  in weight) of rare-earth impurities in KTP crystals grown in self-flux. The dashed line is a free hand correlation intended to emphasise the trend.

quired for efficient optical pumping. It will be shown later, that the optical absorption cross section of Nd can be improved by using W-rich fluxes. This direction must be investigated more thoroughly using RE ions that exhibit the highest distribution coefficients, namely  $\text{Yb}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Er}^{3+}$ .

In view of the fact that the incorporation of RE ions to bulk crystals is limited to rather low concentrations, we have explored the thermal diffusion of  $\text{RE}_2\text{O}_3$  layers deposited by laser ablation on KTP surfaces [5]. The diffusion temperature must be limited to 850°C in order to avoid surface degradation induced by loss of potassium. The presence of structural lattice channels along the *c*-axis of KTP eases the diffusion of RE ions. Nd and Er have been diffused in KTP. The diffusion coefficients along the *c*-axis obtained at 850°C are in the range  $1$ – $5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , which are higher than those obtained for the diffusion of Nd and Er in  $\text{LiNbO}_3$  at much higher temperatures (1027°C), namely  $\approx 0.2$ – $1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . During diffusion, the development of a  $\text{REPO}_4$  phase has been eventually observed on the sample surface. This may stop the diffusion process. Nevertheless, the RE concentrations achieved by this way may reach about  $10^{21} \text{ cm}^{-3}$ . RE impurities have been also incorporated to the KTP lattice by ion implantation [6] and ion beam mixing [7]. Even though the experimental equipment required by these techniques is more complex than that required for thermal diffusion, they have the advantage of involving only relatively low temperatures for sample processing. Undoped KTP thin films have also been prepared by the pulsed laser deposition method [8], but so far the preparation of RE-doped KTP films has not been reported, which makes it a possible future research direction.

### 3. Optical spectroscopy

Due to the low RE impurity concentration in KTP, the room temperature optical absorption is weak, and most of the bands are not well resolved from the background noise. However, the optical absorption of most RE ions has been observed at low temperatures (4.2–77 K). For instance, the

optical absorption and photoluminescence of  $\text{Nd}^{3+}$  [9,10],  $\text{Ho}^{3+}$  [11],  $\text{Tm}^{3+}$  [11] and  $\text{Er}^{3+}$  (reported later in this work) have been studied in KTP. At 4.2 K, the transitions from the lowest energy sublevel of the ground multiplet to the higher energy Stark multiplets can be observed without any contribution from thermally populated sublevels of the ground multiplet. Although this simplifies the spectra, we often found more optical absorption bands than expected from the multiplet splitting in the  $C_1$  symmetry of titanium sites. We presently believe that this fact is associated with the coexistence of RE ions in several environments. In order to show this we shall discuss first the results concerning the spectroscopy of  $\text{Nd}^{3+}$ , and later we will illustrate the situation for the  $\text{Er}^{3+}$  case.

### 3.1. $\text{KTP}:\text{Nd}^{3+}$

Fig. 2 shows a comparison of the 4.2 K optical absorption of  $\text{Nd}^{3+}$  in KTP crystals grown from a self-flux with that observed in crystals grown in a W-rich flux, hereafter KTP(W). Despite the fact that the Nd concentration in both samples was similar, in the former crystals only a well resolved absorption band at 734 nm was observed. Some other minor bands may also be observed, but their weak intensities made their assignment very uncertain.

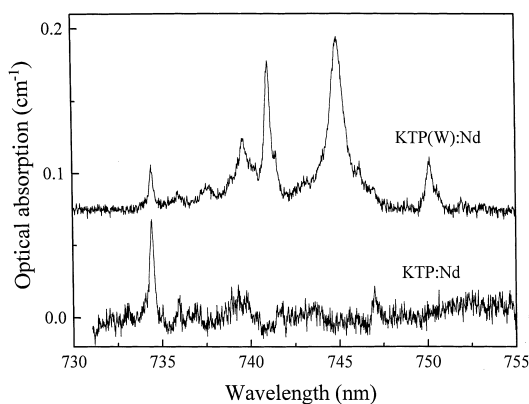


Fig. 2. Comparison of the 4.2 K optical absorption ( ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{7/2} + {}^4\text{S}_{3/2}$ ) of  $\text{Nd}^{3+}$  in KTP crystals grown in a self-flux and in a W-rich flux. The  $\text{KTP(W)}:\text{Nd}$  spectrum has been arbitrarily up-shifted to ease the comparison.

$\text{Nd}^{3+}$  in  $\text{KTP(W)}$  crystals has much higher integrated optical absorption and larger number of observable bands than in KTP. This fact was formerly attributed to a W-induced enhancement of the Nd concentration [9]. However, it is now clear that this is associated to the presence of new Nd centres with higher optical absorption cross sections. The enhancement of the ion absorption cross section is likely due to the reduction in the site symmetry. As  $C_1$  is the site symmetry of titanium sites, where the RE ions are supposed to sit, this would suggest that Nd in KTP has a more symmetric position than the host cations.

The presence of several Nd centres is further supported by the photoluminescence properties of neodymium in KTP and  $\text{KTP(W)}$  crystals. Fig. 3 shows a comparison of the  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$  emission

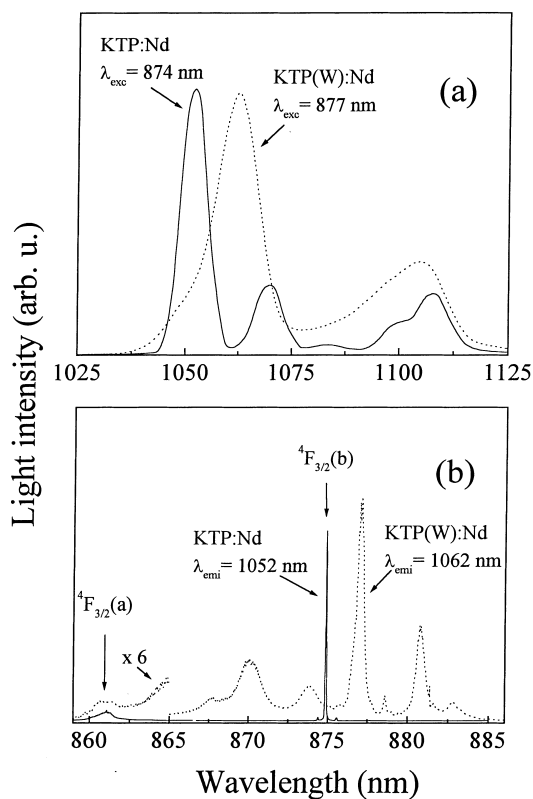


Fig. 3. Comparison of the photoluminescence of  $\text{Nd}^{3+}$  in KTP crystals grown in a self-flux (solid line) and in a W-rich flux (dashed line). (a) 77 K emission spectra. (b) 77 K excitation spectra.

and the corresponding excitation spectra of the  $^4F_{3/2}$  multiplet.  $Nd^{3+}$  in KTP shows several emission bands (solid line in Fig. 3(a)) related to the splitting of the  $^4I_{11/2}$  multiplet. The strongest one peaks at 1051.9 nm. All these emission bands have the same excitation spectrum (solid line of Fig. 3(b)), in which it is possible to observe the splitting of the  $^4F_{3/2}$  multiplet into two sublevels, labelled by  $^4F_{3/2}(a)$  and  $^4F_{3/2}(b)$  in an increasing order in energy. The energy distance between these two sublevels is related to the crystal field strength on the ion.

The emission and excitation spectra of  $Nd^{3+}$  in KTP(W) crystals show the bands observed for  $Nd^{3+}$  in KTP, and in addition a new emission spectrum appears. The new emission spectrum (dashed line of Fig. 3(a)) is characterised by broader bands and the shape of the spectrum slightly depends on the excitation wavelength. The excitation spectrum associated with the latter emission (dashed line of Fig. 3(b)) is also wavelength dependent, and shows several well resolved peaks. These facts suggest the presence of several new centres contributing to the photoluminescence of  $Nd^{3+}$  in KTP(W) crystals.

### 3.2. $KTP:Er^{3+}$ and $RTP:Er^{3+}$

Fig. 4 shows a general overview of the room temperature optical absorption of  $Nd^{3+}$  in KTP

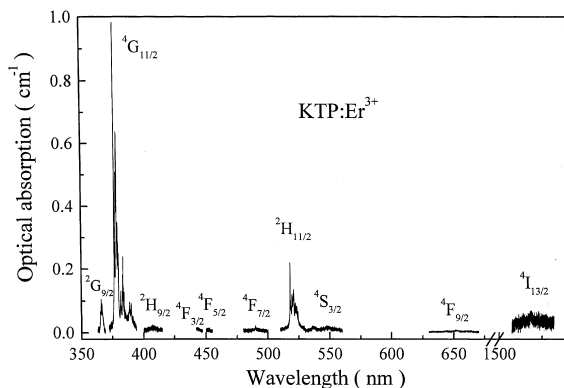


Fig. 4. Room temperature optical absorption of  $Er^{3+}$  in KTP crystals.

crystals. The larger critical concentration and segregation coefficient of Er with respect to Nd allows a more efficient incorporation into the KTP lattice. The erbium concentrations in the KTP and RTP crystals used are  $1 \times 10^2$  and  $4.7 \times 10^2$  ppm respectively. Taken into account the erbium concentration and the differences in the refractive index of both lattices, the line intensities obtained for the  $Er^{3+}$  transitions are similar in KTP and RTP. The exceptions are  $^4G_{9/2}$  and  $^4G_{11/2}$  multiplets which have line intensities about two times larger in KTP than in RTP.

In order to illustrate the coexistence of several centres and the differences found in the two lattices studied, in the following we will discuss the spectroscopic properties of the  $^4S_{3/2}$  multiplet of erbium. The  $^4S_{3/2}$  multiplet may be split by the crystal field into a maximum of two sublevels due to the

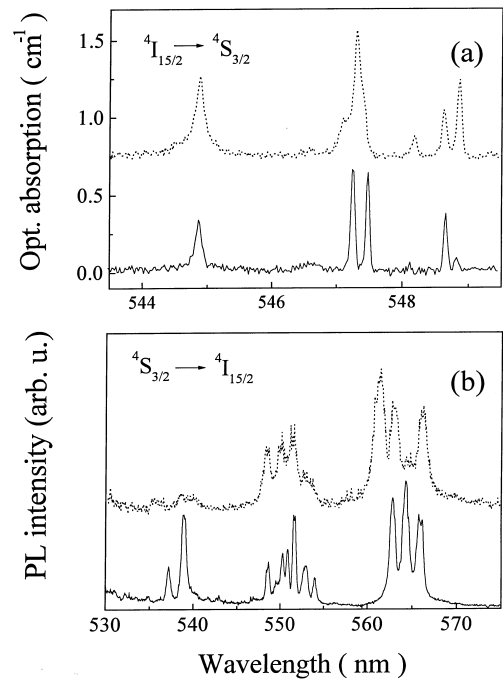


Fig. 5. Optical absorption and photoluminescence of the  $^4S_{3/2}$  erbium multiplet in KTP (solid line) and RTP (dashed line). The RTP spectra have been arbitrary shifted to ease the comparison. (a) Absorption recorded at 4.2 K. (b) Photoluminescence observed at 10 K after excitation of the  $^2H_{11/2}$  level at 518.1 nm.

Kramers degeneracy of the odd electron configuration of erbium. Therefore, a relatively simple optical absorption spectrum may be expected at a low temperature. Contrary to this expectation, Fig. 5(a) shows that at least five bands can be resolved in the 4.2 K optical absorption of  $\text{Er}^{3+}$  in KTP. The erbium spectrum observed in RTP shows bands in the same spectral positions as those observed in KTP, but some additional bands appear.

Fig. 5(b) shows the 10 K photoluminescence corresponding to the  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  emission of  $\text{Er}^{3+}$  in KTP and RTP hosts. To observe the photoluminescence we excited the  ${}^2\text{H}_{11/2}$  level at 518.1 nm. This absorption band is one of the most intense of the erbium spectra in both lattices, and is slightly influenced by the change of the lattice environment. The excitation decays non-radiatively to the  ${}^4\text{S}_{3/2}$  level, and it is expected that all erbium centres present in the sample are excited simultaneously. The comparison of the emission spectra of Fig. 5(b) shows that most of the erbium emission bands in KPT are also present in RPT, but again new emissions are observed in the latter lattice. This is particularly evident with the band peaking at 562 nm.

#### 4. Conclusions and future research directions

Severe limits have been found to the incorporation of rare earth ions into the KTP lattice and some of its isomorphous phases. The RE ions incorporated easier are those having lower ionic radius. The optical absorption and photoluminescence results suggest the presence of several RE-related centres, some of them having much higher absorption cross sections than others. Further improvements of the crystal growth procedures are required to enhance the RE concentration in the crystal, and if possible to select the centres with highest absorption cross sections. The crystal growth of KTP using W-rich fluxes and the study of other isomorphous phases having favourable NLO properties seem promising directions for future research.

The ionic environment of RE impurities in KTP is not presently known with certainty. The growth

experiments suggest that RE impurities substitute titanium. The KTP and RTP lattices have two non-equivalent crystallographic sites for each cation of the crystal [12], therefore at least two different sites may be expected for the RE impurities. This is commonly found for transition metal ions that replace Ti in KTP [13], even though the degree of substitution of the two titanium sites are usually found to be quite different and sensitive to the growth procedure. This shows the multiplicity of impurity centres that the KTP lattice is able to host. The two Ti sites have  $C_1$  symmetry and the lattice environment consists of distorted oxygen octahedra with small differences in the bond angles and distances. Due to the large ionic radius of the trivalent rare-earths in comparison to the  $\text{Ti}^{4+}$ , it seems likely that the RE environment is modified with regard to the Ti site environment, and perhaps a single and quite symmetric type of RE centres may be found in crystals doped with low RE concentrations. However, a multiplicity of perturbed RE centres may arise by the presence of other foreign ions or vacancies close to the RE impurities.

An alternative method to doping of bulk crystals during growth is the incorporation of RE impurities at the sample surface. This method allows to prepare laser sources with a waveguide structure. This is feasible in KTP since the ion exchange technique is well developed to produce optical waveguides [14]. Particular care must be taken to avoid thermal heating of the samples above 850°C, which often leads to a permanent surface modification. The influence of the rare earth impurities on the NLO properties of the host must also be considered. The characterisation of the spectroscopic properties of the ions in bulk crystals is, nevertheless, important to learn about the possible optical performance of RE ions in KTP and as a reference for the optical properties of RE ions incorporated into the surface region.

#### Acknowledgements

This work has been supported by CICyT under project number TIC96-1039.

**References**

- [1] A.J.W. Brown, M.S. Bowers, K.W. Kangas, C.H. Fisher, *Opt. Lett.* 17 (1992) 109.
- [2] K. Kato, M. Masutani, *Opt. Lett.* 17 (1992) 178.
- [3] L.T. Cheng, L.K. Cheng, R.L. Harlow, J.D. Beirlein, *Appl. Phys. Lett.* 64 (1994) 155.
- [4] R. Solé, V. Nikolov, I. Koseva, P. Peshev, X. Ruiz, C. Zaldo, M.J. Martín, M. Aguiló, F. Díaz, *Chem. Mater.* 9 (1997) 2745.
- [5] M.J. Martín, C. Zaldo, M.F. da Silva, J.C. Soares, F. Díaz, M. Aguiló, *J. Phys. Cond. Matter* 9 (1997) L465.
- [6] K. Wang, P. Ding, W. Wang, W.A. Landford, Y. Liu, J. Li, Y. Liu, *Appl. Phys. Lett.* 64 (1994) 3101.
- [7] K. Wang, W. Wang, P. Ding, W.A. Landford, Y. Liu, *J. Appl. Phys.* 77 (1995) 3581.
- [8] P.M. Lundquist, H. Zhou, D.N. Hahn, J.B. Ketterson, G.K. Wong, M.E. Hagerman, K.R. Poepelmeir, H.C. Ong, F. Xiong, R.P.H. Chang, *Appl. Phys. Lett.* 66 (1995) 2469.
- [9] C. Zaldo, M. Aguiló, F. Díaz, H. Loro, *J. Phys. Cond. Matter.* 8 (1996) 10693.
- [10] C. Zaldo, M. Rico, M.J. Martín, J. Massons, M. Aguiló, F. Díaz, *J. Lum.* 79 (1998) 127.
- [11] C. Zaldo, M.J. Martín, R. Solé, M. Aguiló, F. Díaz, P. Roura, M. López de Miguel, *Opt. Mat.* 10 (1998) 29.
- [12] I. Tordjman, R. Masse, J.C. Guitel, *Zeit. Kristall.* 139 (1974) 103.
- [13] J.M. Gaité, J.F. Stenger, Y. Dusausoy, G. Marnier, H. Rager, *J. Phys. Cond. Matter* 3 (1991) 7877.
- [14] J.D. Bierlein, A. Ferreti, L.H. Brixner, W.Y. Hsu, *Appl. Phys. Lett.* 50 (1987) 1216.

Initial page
--------------

Papers
--------