

Chapter 1: **INTRODUCTION**

In December 1958 A.C. Schawlow and C.H. Townes reported that it should be possible to extend the maser principle to the optical frequency part of the electromagnetic spectrum.¹ Only one and a half years later, Mainman demonstrated the first laser.² Since then, the importance of lasers to both science and society has increased dramatically. Today lasers are part of everyday life. Actually, the interest in developing compact blue and green laser sources for data storage and display applications has increased due to promising investigations into wide-gap semiconductor diode lasers,^{3,4} harmonic generation by phase matching in non-linear crystals,⁵ quasi-phase-matching in bulk,⁶ optical fibres and other waveguides,⁷ and up conversion lasers in crystals⁸ and fibers.⁹

1.1. Background.

1.1.1. The self-frequency doubling materials.

In the last ten years, interest has increased in non-linear optical crystals that allow the frequency conversion of coherent light beams in a wide range of wavelengths. When pumped with laser radiations of frequencies ν_1 and ν_2 , non-linear optical materials may generate second harmonic and sum- and difference-frequency mixing of the input radiation.

When an electromagnetic wave propagates through a medium, it is polarized as due to movements of electrons and nuclei in response to the applied field. At low optical intensities, the induced polarisation is proportional to the electrical field of the incident wave and the response of the medium is therefore linear. However, when the intensity of the incident radiation is sufficiently high, non-linear optical interactions can be generated.¹⁰

Compact all-solid-state laser sources (red, green, blue and UV) are needed for a variety of applications such as colour projection, high-density optical data storage, laser printing, medicine, Argon-laser replacement, biofluorescence, underwater communications, stereo lithography, photodynamic therapy....¹¹ A class of these sources is achieved with up-conversion lasers emitting at a shorter wavelength than the pump source.¹² An alternative to up-conversion lasing is frequency conversion by non-linear optical processes such as frequency doubling and sum-frequency mixing.

Non-linear optical crystals with suitable sites for Yb^{3+} and Nd^{3+} ions can combine their 1 μm infrared laser emission of the optically active ions with the second harmonic generation properties of the host to produce green-laser radiation by self-frequency doubling. Attractive crystals for this purpose are multifunction optical materials in which the laser effect and the non-linear optical phenomena occur simultaneously inside the same crystal, thus simplifying the device. A self-frequency doubling laser incorporates fewer reflection, absorption, and scattering losses than conventional intra-cavity frequency doubling systems with separate laser and non-linear crystals such as KTiOPO_4 (KTP), and provides for a simpler and more robust resonator design.¹³

The first lasers of this kind were based on $\text{LiNbO}_3:\text{Tm}^{14}$ and $\text{LiNbO}_3:\text{MgO}:\text{Nd}^{15}$. Today, these systems are efficient and can be diode pumped. The necessary conditions for an optically non-linear crystal to be a self-frequency doubling material are: (i) the crystal must accept fluorescent doping and (ii) the crystal must be phase-matchable for its laser emission. Also, if a material is to be considered a good candidate for power scaling, it should have a high thermal conductivity, high quantum efficiency and a small Stokes factor. To be efficient, the material should have a strong and broad bandwidth pump absorption, as well as a relatively large gain cross-section. So far only a few crystals satisfy these

requirements. These are: LiNbO_3 (LNB), LaBGeO_5 (LBG), $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (BNN), $\beta\text{-Gd}_2(\text{MoO}_4)_3$, $\text{YAl}_3(\text{BO}_3)_4$ (YAB), $\text{CaY}_4\text{O}(\text{BO}_3)_3$ (YCOB) and $\text{CaGd}_4\text{O}(\text{BO}_3)_3$ (GdCOB).

Table 1.1 shows the main results of green self-frequency doubling lasers based on the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ transition of the Nd^{3+} ion. The results for GdCOB:Nd and YCOB:Nd remain below those of YAB:Nd (NYAB). Note the good position of BNN:Nd. Note also that its extrapolation to high pump power is promising. There are other less common channels of self-frequency doubling based on the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ and the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ transitions of the Nd^{3+} ion with emission in red^{16,17} and blue.^{18,19}

Table 1.1. Main results of Nd self-frequency doubling lasers. Reprinted from Brenier, ref. 11, copyright 2000, with permission from Elsevier.

Crystal	Input power (mW)	Output power (mW)	Pumping	Reference
NYAB	870	10	D/CW	Schutz [21]
NYAB	280	3	D/CW	Wang [22]
NYAB	400	69	D/CW	Amano [23]
NYAB	1380	51	D/CW	Hemmati [24]
NYAB	369	35	D/CW	Qiu [25]
NYAB	1600	225	D/CW	Bartschke [26]
NTAB	2200	450	D/CW	Bartschke [26]
LNB:MgO	215	1	Dye	Fan [27]
LNB :MgO	850	18	Dye	Li [28]
LNB:Sc ₂ O ₃	65	0.14	TS/QCW	Yamamoto [29]
LNB:MgO	100	0.2	D/QCW	Ishibashi [30]
LNB:Zn	430	0.65	TS/CW	Capmany [31]
LBG	600	0.09	TS/CW	Capmany [32]
YAB:Nd,Lu	880	24	D/CW	Dekker [33]
BNN	270	46	TS/CW	Kaminskii [34]
YCOB	900	62	D/CW	Eichenholtz [35]
GdCOB	1600	192	TS/CW	Zhang [36]
GdCOB	1250	115	D/CW	Augé [37]

However, these neodymium-lasers have several problems. These include low quantum efficiency, high quantum defects, reabsorption loss in the green and, specially, difficulties with growing the non-linear laser material because of the incorporation of Nd^{3+} ions.²⁰ As a result, self-frequency doubling solid-state lasers based on Nd-doped materials have not had much practical success.

The most promising ion for use in a non-Nd laser in the same range of emission wavelength is Yb^{3+} . This ion has several advantages over Nd^{3+} as the laser-emitting centre because of its very simple energy level scheme, which is made up of only two levels: the ${}^2\text{F}_{7/2}$ ground state and the ${}^2\text{F}_{5/2}$ excited

state. There is no excited state absorption reducing the effective laser cross-section, no up-conversion, no concentration quenching and no absorption in the green, which is extremely favourable for a self-frequency doubling laser. The intense Yb^{3+} absorption lines are well suited for laser diode pumping near 980 nm such as with high-power InGaAs diode lasers, and the small Stokes shift between absorption and emission reduces the thermal loading of the material during the laser operation. Moreover, Yb^{3+} -doped laser crystals with broadband fluorescence allow tunability and subpicosecond-pulse generation in the infrared and the green.³⁸ The disadvantages of Yb^{3+} are that the final laser level is thermally populated, which increases the threshold, and that the operation on a quasi-three-level scheme could produce reabsorption losses and temperature-related effects.³⁹ However, the advantages of using this ion outweigh the disadvantages.

Several highly efficient Yb-lasing in self-frequency doubling materials have been reported.⁴⁰⁻⁵⁰ In all cases, the intensity of the green light generated is quadratically dependent on the incident infrared pumping light. Table 1.2 shows the main results of green self-frequency doubling Yb lasers.

Table 1.2. Main results of Yb self-frequency doubling lasers.

Crystal	Input power (mW)	Output power (mW)	Pumping	Reference
YYAB	2000	1	D/CW	Wang [51,52]
YYAB	1400	160	D/CW	Jiang [53]
YYAB	11000	1100	D/CW	Dekker, Lederer [54,55]
YYAB	4000	270	D/CW	Wang [37]
YYAB	1600	1	D/CW	Wang [52]
LNB:MgO	101	30	TS/CW	Montoya [56]
LNB:MgO	421	58		Montoya [57]
ppLNB:MgO (*)	101	10.5	TS/CW	Capmany [58]
YCOB	1200	357	D/CW	Aron [59]
YCOB	3800	245	HBMLS	Richardson [13]
YCOB	1500	>1	TS/CW	Zhang [46]
YCOB		1	TS/CW	Zhang [60]

(*) ppLNB:MgO → periodically poled LiNbO_3 :MgO

The low green output power obtained with GdCOB may be due to the broad emission spectra and the short length of the crystal.^{48,61} Druon et al.⁶¹ generated 90-fs pulses of green light in this material. Until then, exclusively Yb^{3+} -doped glass lasers had produced pulse widths of below 100 fs. In YCOB, the self-frequency doubling efficiency was low because the laser bandwidth was larger than the angular acceptance bandwidth.⁴⁶ Lederer et al.⁵⁵ reported the first semiconductor saturable absorber mirror (SESAM) cw mode-locked, diode-pumped Yb:YAB laser to produce picosecond pulses in the

green. Dekker et al.⁵⁴ reported that power scaling a miniature self-frequency doubling laser based on this material is possible and can produce record powers of 1.1 W CW green.

Quasi-phase-matching structures have several advantages over Yb³⁺-doped single domain materials. When tested in periodically poled LiNbO₃:MgO:Yb,^{62,63} the green radiation was always present during the laser action. Also, the second harmonic generated signal was substantially wider than that obtained with a self-frequency doubling with a single-domain Yb-doped LiNbO₃:MgO crystal of similar length.³⁹ This opens up the possibility of tunability. Yb³⁺-based lasers can be tuned within a certain spectral range because the ion-lattice coupling of the 4f electrons is stronger than that of other rare earth ions.⁶⁴

1.1.2. The structural field of KTiOPO₄.

Since it was introduced as a non-linear optical material in 1976,⁶⁵ potassium titanyl phosphate (KTiOPO₄ or KTP) has attracted considerable attention as a medium in applications that require a high degree of second-order susceptibility.⁶⁶ KTP has been established as a unique inorganic material because its exceptional properties for several non-linear optical applications^{67,68} including sum and difference frequency mixing⁶⁹⁻⁷¹ and optical parametric oscillation.⁷²⁻⁷⁷ In particular, KTP is the material of choice for frequency doubling Nd-lasers at 1 μm radiation.^{65,78-80}

KTiOPO₄ single crystals are chemically inert and relatively easy to grow.⁸¹ KTP's optical window extends from 0.35 to 4.5 μm.⁸² It has practical value as a non-linear and electrooptical material because it combines large optical non-linearity and electrooptic coefficients, a high optical-laser-induced damage threshold,⁷⁹ good phase-matchability, a large temperature window,^{83,84} an extremely low onset power threshold,⁸⁵ high power conversion efficiency and high optical homogeneity with a suitable transparent wavelength range and low dielectric constants. KTP crystals have been used as parametric amplifiers for generating picosecond tuneable infrared radiation.⁸⁶ Pump wavelength tuning of optical parametric oscillations and frequency mixing have been examined,⁸⁷ and high-repetition-rate femtosecond optical parametric oscillation has been reported.⁸⁸⁻⁸⁹ Also, sum frequency mixing of red and infrared radiation to generate green light has been studied, and efficient and tuneable parametric superfluorescence has been demonstrated.⁹⁰ In addition, high density optical recording has been achieved,⁹¹ and a 20 W average-power KTP intracavity-doubled Nd:YAG laser has been developed.⁹² Also, noncritically phase-matched KTP crystals at room temperature have been analysed for potential applications in the laser tuning of diode-pumped systems,⁹³⁻⁹⁴ and the production of blue light for compact laser sources from the frequency doubling of small diode lasers.⁹⁵⁻⁹⁶

KTP belongs to a highly diverse and versatile structural family.⁹⁷ By the inclusion host-guest relationship and two formula units in the asymmetric unit, with all the available atoms in general

positions, a large number of synthetic permutations of the KTP structure are possible. It is said that doping KTP clearly affects some of the physical properties of the resulting solid phase. Understanding the structure-property relationships in KTP led to the design of new materials and the fine tuning of single-crystal properties. In conjunction with its isomorphs, KTP offers exceptional versatility for device design. Several studies aimed at improving the properties of KTP single crystals by doping and finding newer applications have focused on arresting the high ionic conductivity,⁹⁸⁻¹⁰¹ improving the phase matching conditions for second harmonic generation,¹⁰²⁻¹⁰⁴ and enhancing the transparency,^{98,100,105,106} etc.

We can describe this family of compounds as materials with the general formula $ABOXO_4$ where $A = K, Rb, Na, Cs, Tl, NH_4$; $B = Ti, Sn, Sb, Zr, Ge, Al, Cr, Fe, V, Nb, Ta$; and $X = P, As, or Si$, which crystallizes in the orthorhombic system, space group $Pna2_1$.^{107,108} Both aliovalent and monovalent substitutions are possible. The guest framework comprises A ions and the host framework comprises the extended helical network of BO_6 octahedra bridged by X atoms. In the $ABOXO_4$ structural field, the behaviour of the A cations determines the ferroelectric properties, while the BO_6 octahedra together with the A cations contribute considerably to the non-linear optical properties. Wrong choices of A, B, and X can dramatically affect the non-linear optical behaviour. Figure 1.1 shows the structure field for $KTiOPO_4$ isomorphs in which at least one ion has been completely replaced. Projecting the structure field onto the B and X axes clearly shows, first, that the smaller the A ion, the smaller the B and X ions that can be completely substituted into the host, and second, the larger the A ion, the larger the B and X ions that can be completely substituted into the host. Over 100 isomorphous derivatives of KTP have been created,^{67,68,102-119} and this number increases every year.

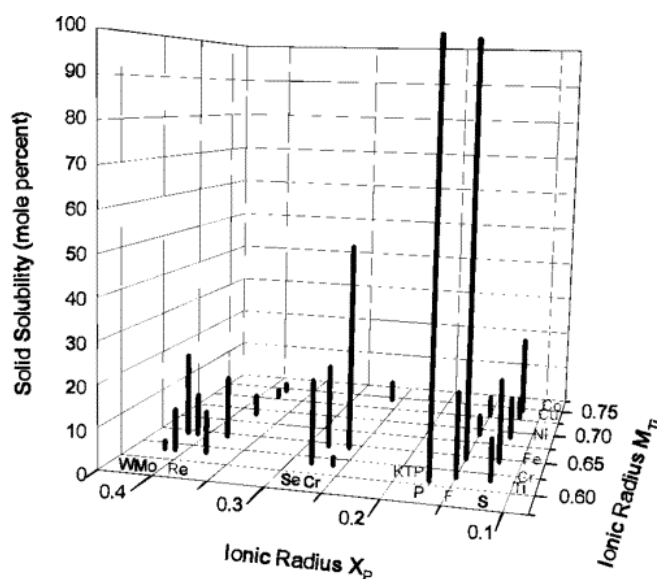


Figure 1.1. Solid solubility versus ionic radii M_x , X_p dopant ion pairs on the octahedral position in KTP. Reprinted with permission from *Chem. Mater.* **1996**, *8*, 248-256. Copyright 1996 American Chemical Society.

Interest has recently shifted to doping KTP with rare earth ions^{104,120,121} in order to induce second harmonic generation for fundamental wavelengths of under 990 nm and produce a self-frequency doubled output.

1.1.3. The precedents of doping KTiOPO_4 isostructurals with lanthanide ions.

So far the main fields in which KTP and isostructurals doped with lanthanide ions have been investigated are waveguides, waveguide lasers and bulk crystals.¹²²⁻¹²⁴

1.1.3.1. Crystal growth and surface modifications.

Several techniques have been used for the crystal growth of Ln-doped KTP (Ln = Nd, Ho, Er, Tm, Tb and Yb). One of these is the Top-Seeded Solution Growth (TSSG) slow-cooling technique^{120,121,124,125} (see [paper I](#)). The incorporation of Ln ions into the KTP lattice using this technique has two limitations. Firstly, Ln ions in the melted flux induce the nucleation of new phases, namely LnPO_4 and $\text{K}_3\text{Ln}(\text{PO}_4)_2$, and the KTP nucleation region narrows. Above a certain critical Ln concentration in the starting flux, the KTP phase does not nucleate. Secondly, the distribution coefficient of Ln ions in KTP can be low, depending on the ionic radius of the Ln ions (see Figure 1 in [paper I](#)). These limitations mean that the Ln concentration in bulk crystals is 50-600 ppm ($\approx 5 \times 10^{17} - 6 \times 10^{18} \text{ cm}^{-3}$), which is well below the concentrations used in Ln-doped laser matrices (which are typically in the 10^{20} - 10^{21} cm^{-3} range). Using codoping elements with Ln doping generally increases the distribution coefficient of the lanthanide.¹²⁰ The results are best when the codoping elements are Rb^+ and Nb^{5+} . To enhance the incorporation of Ln to the KTP lattice, it seems that codoping should be done using an element whose ionic radius is as close as possible to that of the element to be substituted, but whose charge is greater.

The most likely sites for Ln in the KTP lattice are the Ti-site and the K-site. The fact that the distribution coefficient of the rare earth ion decreases as its ionic radius increases (see Figure 1 in [paper I](#)) suggests that Ln^{3+} ions substitute the Ti^{4+} of the lattice.

Because the incorporation of Ln ions to bulk crystals grown by high temperature solutions is limited to rather low concentrations, the thermal diffusion of Ln_2O_3 layers deposited by laser ablation on KTP surfaces has also been explored.¹²⁵ The results obtained with this technique are also shown in [paper I](#). The most significant conclusions are: (i) the diffusion temperature must be limited to 850°C in order to avoid surface degradation induced by loss of potassium; (ii) the structural channels along the c -axis of KTP^{80} ease the diffusion of Ln ions, so diffusion coefficients at 850°C are in the $1\text{-}5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ range, which is higher than the range for LiNbO_3 at much higher temperatures; and (iii) during

diffusion, the development of a LnPO_4 phase is eventually observed on the sample surface. This may stop the diffusion process. Nevertheless, the Ln concentration achieved in this way may reach about 10^{21} cm^{-3} .

Ln impurities have been also incorporated into the KTP lattice by ion implantation and ion beam mixing.^{122,123,126-136} Er^{3+} ,^{122,123,128-136} Yb^{3+} ,^{123,128,134} and Tm^{3+} ,^{134,135} for example, have been implanted in KTP. The damage caused by ion implantation in the sample strongly depends on the mass of the implanted ion, the energy and the dose at which the ion was implanted, and the annealing process to which the implanted sample was subjected.¹²⁸ To test the benefits of annealing on the sample, several experiments have been performed, including furnace annealing in N_2 ,^{128,129,133,135} furnace annealing in Ar ambient,¹²³ rapid thermal annealing in Ar-atmosphere,¹²⁹ furnace annealing in flowing oxygen atmosphere (annealing in oxygen improves the transparency of $\text{KTP}^{106,130,131}$) and annealing in a quartz ampoule filled with oxygen and K_2O salt, which leads to an overpressure of K_2O .¹³¹ The results were best when the annealing was performed in K_2O atmosphere. Here damage annealing was complete, there was no material decomposition and there was a partial substitutional incorporation of the Ln atoms.¹³¹

Pulsed laser deposition is an attractive alternative for incorporating Ln into KTP with a high level of concentration.¹³⁶ Only Er has been incorporated into KTP by this method. A smooth, transparent, and shiny surface with a maximum Er concentration of 3 at. % was obtained, but its distribution was not uniform.

Another method for producing KTP doped with Er^{3+} is electron-beam evaporation with subsequent irradiation with an Ar^+ beam. With this method a maximum of 2.88% of Er was obtained.¹²²

Anderson et al.¹⁰⁴⁻¹⁰⁵ doped RbTiOAsO_4 (RTA) with lanthanide ions by hydrothermal and solid state synthesis. RTA:Ln,X crystals with $\text{Ln} = \text{Yb, Gd, Ho, Er and Lu}$, and with $\text{X} = \text{Nb, Sb, Re, W, Mo, Ca, Sr, Ba, Pb, S, Cl, F and Se}$ were grown¹⁰⁴ in order to modify the dispersion curves of this material and allow a frequency doubling of less than 990 nm without using sum frequency mixing,⁸⁴⁻⁸⁵ cascade tripling,¹³⁷ or guided waves.¹³⁸⁻¹⁴¹ Solid solubilities in RTA were low.¹⁰⁵ To increase Ln solubility, several experiments examined the substitution of Rb by Cs, but mixed phases or very small amorphous particles were obtained.¹⁰⁵

At the starting point of this work in FiCMA's laboratory, RbTiOPO_4 (RTP) doped with Er^{3+} was also grown by Top-Seeded Solution Growth.¹²¹ Although the concentration of Er^{3+} in these crystals was higher than with KTP, it was not high enough to obtain efficient luminescence from the lanthanide ion.

1.1.3.2. Optical characterisation of lanthanide ions in $KTiOPO_4$ and isostructurals.

Wang et al. demonstrated the availability of Er implanted KTP in waveguiding. They observed fourteen dark modes and measured the refractive index for the KTP waveguide.¹³³

The second harmonic intensities for RTA:Ln,Nb decreased in the order Yb>Gd>Ho>Er>Lu, which is very similar to the order in which the ionic sizes of the trivalent ions decrease (Gd>Ho>Er>Yb>Lu) and this was attributed to the smaller overlap of metal $d\pi$ and oxygen $p\pi$ orbitals when the metal d orbitals are partially filled, and to the interruption of the extended Ti-O-Ti-O chains by dopant metal atoms on the Ti site.¹⁰⁵

As it is very difficult to incorporate lanthanides into the crystal lattice, the spectroscopic properties of these ions in these materials have been considered only recently. It is also difficult to determine the optical properties of the lanthanide ions incorporated in thin films because of their thickness. On the other hand, the emission properties of these ions can be strongly modified by the presence of lattice defects induced by the implantation process. The determination of the optical absorption and emission properties of bulk KTP:Ln is therefore of interest as a reference for KTP:Ln thin-film related devices.¹⁴²

Because the Ln concentration in KTP is low, 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 Ln ions has been observed at low temperatures (4.2-77K). For instance, the optical absorption and photoluminescence of Nd^{3+} ,^{143,144} Ho^{3+} ,¹⁴² Tm^{3+} ¹⁴² and Er^{121,131,133,136} have been studied in KTP. The most important of these results are shown in [paper I](#). There were more optical absorption bands than expected from the multiplet splitting in the C_1 symmetry of titanium sites for all Ln studied. This has been associated with the coexistence of Ln ions in several environments.

KTP(W):Nd crystals have a higher integrated optical absorption and more bands than KTP:Nd crystals (see Figure 2 in [paper I](#)). This has been related to the presence of new Nd centres with higher optical absorption cross-sections due to the reduction of symmetry in the structural site.

The emission and excitation spectra of Nd^{3+} in KTP(W) crystals show the bands observed for Nd^{3+} in KTP. There is also a new emission spectrum that is characterized by broader bands (see Figure 3 in [paper I](#)). The shape of the spectrum depends slightly on the excitation wavelength, as well as the excitation spectrum associated with the latter emission. These facts suggest that several new centres contribute to the luminescence of Nd^{3+} in KTP(W) crystals.

Ho^{3+} and Tm^{3+} are interesting for eye-safe laser devices, because their laser emissions are close to 2 μm ,¹⁴⁵ and for solid state minilaser devices.¹⁴⁶ Because the concentration of Ho^{3+} in KTP was low, the limited size of the samples available and the signal to noise ratio in the infrared was small, its optical absorption bands couldn't be determined.¹⁴² In the photoluminescence studies of Tm^{3+} in

KTP,¹⁴² several overlapped emission bands were observed in the 1100-1400 nm (7150-9100 cm⁻¹), 750-850 nm (11750-13300 cm⁻¹) and 640-700 nm (14300-15625 cm⁻¹) spectral regions. These corresponded to the $^3H_6 \rightarrow ^3H_5$, $^3F_4 \rightarrow ^3H_6$, $^1G_4 \rightarrow ^3H_5$ and $^1G_4 \rightarrow ^3H_4$ transitions, respectively.

The concentrations of erbium in the KTP and RTP crystals obtained in [paper I](#) were 1×10^2 and 4.7×10^2 ppm, respectively and the line intensities for the Er³⁺ transitions were similar. The exceptions were $^4G_{9/2}$ and $^4G_{11/2}$ multiplets, whose intensities in KTP were about two times larger than they were in RTP. However, the spectrum in the RTP sample was well defined and eight multiplets could be resolved, while only four could be reliably resolved from the noise in KTP¹²¹ (see Figure 4 in [paper I](#)).

Most of the erbium emission bands in KTP were also present in RTP, but there were new emissions in RTP (see Figure 5 in [paper I](#)). The photoluminescence emission of Er³⁺ corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition could only be observed in KTP and RTP at 5 K. In KTP the spectrum agreed well with the presence of eight overlapped bands, but in RTP the spectrum had more resolved bands.

The photoluminescence intensity of Er³⁺ in Er-implanted KTP samples near 1530 nm has been also studied^{131,133,136} (see Figure 1.2). It was found that the photoluminescence intensity decreased as the temperature increased.

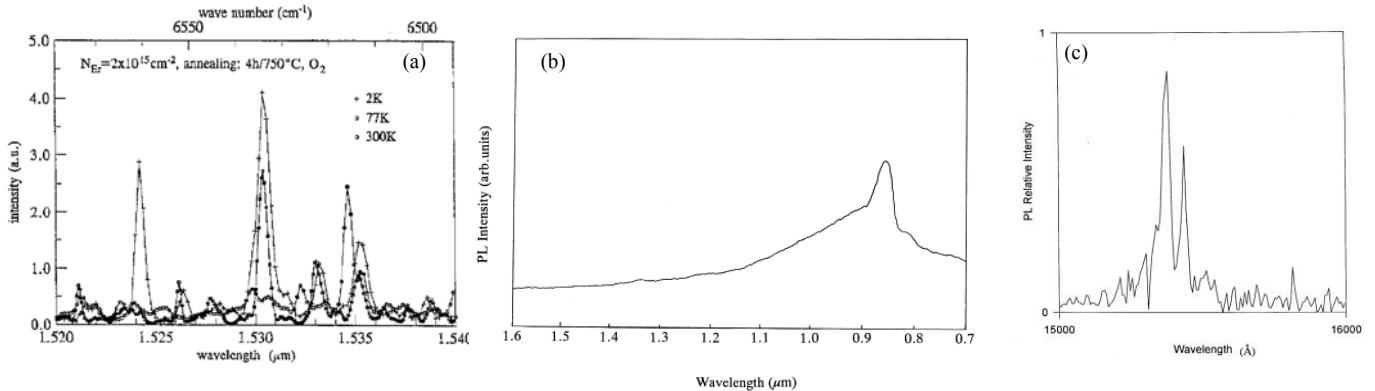


Figure 1.2. Luminescence spectra of Er³⁺ in KTP implanted samples. (a) Reprinted from Opfermann et al. ref. [131](#), copyright 1997, with permission from Elsevier; (b) reprinted from Wang et al. ref. [133](#), copyright 1998, with permission from Elsevier; and (c) reprinted with permission from Wang et al. ref. [136](#), copyright 1998, American Institute of Physics.

1.2 The aim of this Doctoral Thesis

To date, KH₂PO₄ (KDP), LiB₃O₄ (LBO), β-BaB₂O₄ (β-BBO) have been used for the second harmonic generation (SHG) of Nd-type lasers to generate green light.¹⁴⁷ However, all these materials

have some limitations, such as the maximum available size, hygroscopicity or a low harmonic conversion efficiency. The last decade has established KTP as a superior alternative to these materials for this application. And, if KTP can be doped with Ln, its potential applications will increase because this may produce a self-frequency doubling material. As we saw in the previous section, the incorporation of lanthanide ions into the KTP lattice and some of its isomorphous crystals is strictly limited. Further improvements in the crystal growth procedures are needed to enhance the Ln concentration in this family of crystals. The study of other isomorphous phases with favourable non-linear optical properties seems to be a promising area for future research. Despite the long history of harmonic generation, it is therefore not surprising that there is still room for new non-linear optical crystals to mitigate these limitations.¹⁴⁸

This is how this work is included, as we can see in the *Conclusions and Future Research* section in [paper I](#). A new non-linear material is developed that solves some of the problems of the crystals that are used most often today in this field and that could be used as self-frequency doubling crystal. As we explained before, substituting K^+ with Rb^+ in the KTP structure enhances the Ln concentration in the crystals.¹²¹ Using Nb^{5+} as codopant also enhanced the Ln concentration in KTP,¹²⁰ so combining both of these effects, i.e. substituting K^+ with Rb^+ and using Nb^{5+} as codopant, to obtain RTP:(Nb,Ln) crystals seemed a good way to obtain a concentration of Ln in the crystals that was high enough to produce an efficient laser emission.

The method chosen to grow these crystals was the TSSG technique because they decompose before melting, they melt incongruently. This technique has several advantages over the other doping techniques listed in the previous section. Using this technique we can avoid the surface degradation and formation of $LnPO_4$ phases that occur with thermal diffusion, the crystal is not damaged as it is with ionic implantation, OH^- is not present as it is with hydrothermal techniques, and we can grow bulk crystals and not just films on a surface as with all the others techniques, except hydrothermal growth.

Niobium was also chosen as an ion to balance the charge in the substitution of Ti^{4+} by Ln^{3+} because of its high polarisability and the favourable non-linear response it imparts in other solid-state oxides,¹⁴⁹ such as $KNbO_3$,¹⁵⁰ $LiNbO_3$ ¹⁵¹ and $Ba_2NaNb_5O_{15}$. On the other hand, a cut-off wavelength reduction of up to 100 nm was achieved by doping KTP with Nb.¹⁰³ This allows these crystals to be used for frequency doubling below the limit of 980 nm of pure KTP. The effect is expected to be similar for RTP:Nb crystals.

We chose Er^{3+} and Yb^{3+} , the doping of which has been extensively studied in many matrixes to obtain laser radiation of around $1.5 \mu m$ ¹⁵² and $1 \mu m$,¹⁵³⁻¹⁵⁵ respectively. There is interest in Er^{3+} for applications in optical communications at long distances. This is because of its efficient emission near the region of optical losses in silica fibres ($1.5 \mu m$), which is attributed to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition.¹⁵⁶ One interesting application in medicine is the $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition, which emits around $2.8 \mu m$.¹⁵⁷

We also chose Er^{3+} because of its middle ionic radius in the lanthanide family, which can provide an accurate idea of how this family of ions behaves in these crystals. The benefits of Yb^{3+} are extensively explained in Section 1.1 of this Introduction. Clearly, we chose Yb^{3+} in order to develop a new self-frequency doubling solid-state laser based on this ion.

To achieve this, I have studied the crystal growth, and the structural and optical characterisation of RTP:(Nb,Ln) crystals in this Thesis.

The ionic environment of Ln ions in KTP and isomorphous crystals is not yet known with certainty, but growth experiments suggest that Ln substitutes titanium. The KTP lattice has two non-equivalent crystallographic sites for each cation of the crystal,¹⁵⁸ so we may expect at least two different sites for the Ln ions. This has often been found for transition metal ions that replace Ti in KTP,¹⁵⁹ even though the degrees of substitution of the two titanium sites are usually quite different and sensitive to the growth procedure. As the ionic radius of the trivalent lanthanides are larger than that of the Ti^{4+} , it is likely that the Ln environment is different from the Ti environment, and a single and quite symmetric type of Ln centre may be found in crystals doped with low Ln concentrations. However, there may be a multiplicity of perturbed Ln centres because of the presence of other foreign ions or vacancies close to the Ln impurities.

To clarify these assumptions, in this Thesis we carried out structural characterisation studies on RTP:(Nb,Ln) crystals (Ln = Er and Yb). We think that these results can easily be extrapolated to the other KTP isostructurals also doped with Ln.

Lanthanide ions in KTP or its isomorphs may influence the properties in the areas between the fundamental and the second harmonic of Nd:YAG laser radiation. The influence of the lanthanides on the non-linear optical properties of the host must therefore also be considered, and the characterisation of the spectroscopic properties of the ions in bulk crystals is important for determining the possible optical performance of Ln ions in RTP:Nb crystals. All these studies have been done in order to possibly obtain a new self-frequency doubling material.

[Initial Page](#)

[Table of Contents](#)