# Crystal growth, optical characterisation and laser operation of $Yb^{3+}$ in monoclinic double tungstates

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**ABSTRACT**

This thesis focuses on the crystal growth and the compositional, structural, morphological and optical characterisations of the monoclinic phase of the double tungstates belonging to the family of $K(RE^{3+})(WO_4)_2$, where $RE^{3+}$ denotes $Y^{3+}$, $Gd^{3+}$, $Yb^{3+}$, $Er^{3+}$ and $Lu^{3+}$, which are doped with $Yb^{3+}$ and $Er^{3+}$ ions for laser emission generation.

The interest and originality of the scientific work, both in different areas of Physics and Chemistry and in a multidisciplinary approach, lie in the crystal growth, the spectroscopic characterisations, and ultimately in the laser action because these new laser crystals are extremely promising for diode-pumped high-power lasers.

The manuscript is divided into 5 chapters. The first chapter, naturally, is the introduction, which explains the current research position in the context of solid-state laser materials. Chapter 2 describes the apparatus for growing single crystals by the Top-Seeded Solution Growth (TSSG) method, which is suitable for growing such tungstates, and the experimental techniques for the characterisation of our materials. Chapters 3 and 4 describe the crystallisation, crystal growth, crystallographic, optical and spectroscopic properties of the un-doped and rare earth-doped tungstates under study. The spectroscopic characterisation of the active ions, to optimise luminescence observation of $Yb^{3+}$ (infrared emission at around 1025nm) and $Er^{3+}$ (infrared Stokes and visible Anti-Stokes emissions at around 1550nm and 500nm, respectively) involved the most detailed work in this thesis. The final chapter presents the conclusions of our research work on $Yb^{3+}$ laser generation in stoichiometric $KYb(WO_4)_2$ and $KLu(WO_4)_2$ grown crystals carried out in collaboration with the laboratories of the *Max-Born Institute for Nonlinear Optics and Ultrafast Spectroscopy* in Berlin. This completed study for Ti:sapphire and diode-pumped lasers was highly successful.

**PREFACE**

The Ph. D. work contained in this Thesis was carried out at the group of *Física i Cristal·lografia de Materials* (FiCMA), in the *Department of Physical and Inorganic Chemistry of the Rovira i Virgili University* in Tarragona (Spain) between March 2000 and March 2004, directed by Professor Francesc Díaz and Dr. Jaume Massons.

Within the framework of this Thesis, we have collaborated actively with the following research groups: Dr. V. Nikolov at the *Bulgarian Academy of Sciences* (Sofia, Bulgaria); Prof. C. Zaldo at the *Instituto de Ciencia de Materiales de Madrid* (Cantoblanco, Spain); Prof. X. Solans at the *University of Barcelona* (Barcelona, Spain); Prof. G. Boulon at the *Claude Bernard University* (Lyon, France) and Dr. V. Petrov and Dr. U. Griebner at the *Max-Born Institute for Non-linear Optics and Ultrafast Spectroscopy* (Berlin, Germany).

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A scientific study involves team-work in which comments and contributions are of great value. It is always useful, and indeed necessary, to discuss ideas and the results of a project with others. In this way one receives criticism of the part of the work one is personally involved in. A doctoral thesis is no exception, and PhD students undoubtedly need support not only from their supervisors, but also from the senior researchers around them, who are, of course, more expert in the discipline.

I would like, therefore, to acknowledge the scientific knowledge that I have acquired over these years.

Firstly, I would like to thank my thesis directors, Professor Francesc Díaz and Dr. Jaume Massons, for giving me the opportunity to join the Physics and Crystallography of Materials (FiCMA) group of the Rovira i Virgili University and prepare my doctoral thesis. I am grateful for everything I have learnt from them. I would also like to add that I will always be willing to help them on any matter if at all possible.

Secondly, I would like to thank the other member of the FiCMA group, Professor Magdalena Aguiló, Dr. Josefina Gavaldà and Dr. Rosa Solé, for the support they have given me over the last few years and from whom I have learnt a great deal. Many thanks also to Dr. Xavier Ruiz for the friendly conversations we have had and for the pleasant moments we have shared during lectures. The support of the other members of the FiCMA group, the technicians, Mr. Agustí Montero and Ms. Nicolette Bakker, has also been invaluable.

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From outside the scientific field, I would very much like to acknowledge the moral support from my close family (Domingo, Josefa, David, Raul, Ricard, Alejandro, Andreu

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Finally, I would like to thank my mother and father, who fostered my interest in science from a young age and never wavered in their support for the path I have chosen. I would not be who I am without the many opportunities they have given me in my life.

*To my close family and*
*to Miriam,*

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## List of publications

The results of this Doctoral Thesis are based on the work contained in the following papers.

**Paper I:** Pujol, M.C.; **Mateos, X.**; Solé, R.; Gavaldà, Jna.; Massons, J.; Aguiló, M.; Díaz, F. "Linear Thermal Expansion Tensor in $KRE(WO_4)_2$ (RE=Gd,Y,Er,Yb) Monoclinic Crystals." *Materials Science Forum,* **378-381**, 710-717 (2001).

**Paper II:** Pujol, M.C.; **Mateos, X.**; Solé, R.; Massons, J.; Gavaldà, Jna.; Solans, X.; Díaz, F.; Aguiló, M. "Structure, crystal growth and physical anisotropy of $KYb(WO_4)_2$, a new laser matrix." *Journal of Applied Crystallography,* **35**, 108-112 (2002).

**Paper III:** Pujol, M.C.; Bursukova, M; Güell, F.; **Mateos, X.**; Solé, R.; Gavaldà, Jna.; Aguiló, M; Massons, J.; Díaz, F.; Klopp, P.; Grieber, U. and Petrov, V. "Growth, optical characterization and laser operation of a stoichiometric crystal $KYb(WO_4)_2$." *Physical Review B,* **65**, 165121:1-11 (2002).

**Paper IV: X. Mateos**, R. Solé, Jna. Gavaldà, M. Aguiló, J. Massons and F. Díaz. "Crystal growth, optical and spectroscopic characterisation of monoclinic $KY(WO_4)_2$ co-doped with $Er^{3+}$ and $Yb^{3+}$. " *Optical Materials* (2004), in press.

**Paper V: X. Mateos**, C. Pujol, F. Güell, M. Galán, R. Solé, Jna. Gavaldà, M. Aguiló, J. Massons and F. Díaz. "Erbium spectroscopy and 1.5 μm emission in $KGd(WO_4)_2$:Er,Yb single crystals." *IEEE Journal of Quantum Electronics*, **40**, 759-770 (2004).

**Paper VI: X. Mateos**, V. Petrov, M. Aguiló, R. Solé, Jna. Gavaldà, J. Massons, F. Díaz, U.Griebner. "Continuous Wave Laser Oscillation of $Yb^{3+}$ in Monoclinic $KLu(WO_4)_2$." *IEEE Journal of Quantum Electronics*, **40**, 1056-1059 (2004).

**Paper VII:** **X. Mateos**, F. Güell, M.C. Pujol, M. A. Bursukova, R. Solé, Jna. Gavaldà, M. Aguiló, F. Díaz and J. Massons. "Green luminescence of $Er^{3+}$ in stoichiometric $KYb(WO_4)_2$ single crystals." *Applied Physics Letters*, **80**, 4510 (2002).

**Paper VIII:** **X. Mateos**, M.C. Pujol, F. Güell, R. Solé, Jna. Gavaldà, J. Massons, M. Aguiló and F. Díaz. "Infrared-to-green up-conversion in $Er^{3+}$,$Yb^{3+}$ -doped monoclinic $KGd(WO_4)_2$ single crystals." *Optical Materials* (2004), in press.

**Paper IX:** **X. Mateos**, M. C. Pujol, F. Güell, R. Solé, Jna. Gavaldà, M. Aguiló, F. Díaz and J. Massons. "Sensitization of $Er^{3+}$ emission at 1.5 μm by $Yb^{3+}$ in $KYb(WO_4)_2$ single crystals" *Physical Review B,* **66**, 214104 (2002).

**Paper X:** **X. Mateos**, R. Solé, Jna. Gavaldà, M. Aguiló, J. Massons, F. Díaz, U. Griebner and V. Petrov. "Crystal growth, spectroscopic investigations and laser operation of $Yb^{3+}$ -doped potassium lutetium tungstate", *Optical Materials* (2004), submitted.

**Paper XI:** **X. Mateos**, R. Solé, Jna. Gavaldà, M. Aguiló, J. Massons and F. Díaz. "Ultraviolet and visible emissions of $Er^{3+}$ in $KY(WO_4)_2$ single crystals co-doped with $Yb^{3+}$ ions." *Journal of Luminescence*, (2004) submitted.

**Paper XII:** **X. Mateos**, R. Solé, Jna. Gavaldà, M. Aguiló, J. Massons and F. Díaz. Ultraviolet and visible emissions of $Er^{3+}$ in monoclinic $KYb(WO_4)_2$ single crystals." *IEEE Journal of Quantum Electronics*, (2004) submitted.

**Paper XIII:** P. Klopp, U. Griebner, and V. Petrov, **X. Mateos**, M. A. Bursukova, M. C. Pujol, R. Solé, Jna. Gavaldà, M. Aguiló, F. Güell, J. Massons, T. Kirilov, and F. Diaz. "Laser operation of a new stoichiometric crystal $KYb(WO_4)_2$", *Applied Physics B*, **74**, 185 (2002).

## Other publications by the author related to the subject but not included in this thesis

**Paper XIV:** M. Rico, M.C. Pujol, **X. Mateos**, J. Massons, C. Zaldo, M. Aguiló and F. Díaz. "Yb sensitising of $Er^{3+}$ up-conversion emission in $KGd(WO_4)_2$:Er:Yb single crystals." *Journal of Alloys and Compounds*, **323-324**, 362 (2001).

**Paper XV**: Pujol, M.C., Güell, F., **Mateos, X.**, Gavaldà, Jna., Solé, R., Massons, J., Aguiló, M. and Díaz., F. "Crystal growth and spectroscopic characterisation of $Tm^{3+}$ -containing $KYb(WO_4)_2$ single crystals." *Physical Review B.***66**, 144304 (2002).

**Paper XVI: Mateos, X.**; Güell, F.; Díaz, F.; Massons, J. "Láseres verdes y azules" *Mundo Científico*, september (2002)

**Paper XVII:** F. Güell, **X. Mateos**, Jna. Gavaldà, R. Solé, M. Aguiló, F. Díaz and J. Massons. "Blue luminescence in $Tm^{3+}$ -doped $KGd(WO_4)_2$ single crystals" *Journal of Luminescence*, **106**, 109 (2004).

**Paper XVIII:** F. Güell, **X. Mateos**, Jna. Gavaldà, R. Solé, M. Aguiló, F. Díaz, M. Galan and J. Massons. "Optical characterization of $Tm^{3+}$ -doped $KGd(WO_4)_2$ single crystals" *Optical Materials*, **25**, 71 (2004).

**Paper XIX:** I. Nikolov, **X. Mateos**, F. Güell, J. Massons, V. Nikolov, P. Peshev and F. Díaz. "Optical properties of $Cr^{3+}$:$NaAl(WO_4)_2$ crystals, a new candidate for broadband laser applications" *Optical Materials,* **25**, 53 (2004).