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A new self-doubling material: $\text{RbTiOPO}_4:(\text{Nb},\text{Ln})$

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Abstract

Concentrations of Er^{3+} and Yb^{3+} of 0.65×10^{20} and 1.95×10^{20} atoms cm^{-3} , respectively, have been obtained in $\text{RbTiOPO}_4:\text{Nb}$ (RTP:Nb) crystals. Some of the Er^{3+} and Yb^{3+} spectroscopic properties in RTP:Nb crystals are discussed to illustrate the contribution of different centres to the optical absorption and photoluminescence properties. The second harmonic generation capability of crystals containing Nb slightly increase with respect to RTP and a strong dependence was observed with the ratio between the concentration of Nb and lanthanide in them. All these results open the possibility of obtaining a new self-doubling material.

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1. Introduction

Rubidium titanyl phosphate RbTiOPO_4 (hereafter RTP), like KTiOPO_4 (KTP), has high non-linear optical and electrooptical coefficients, high optical damage threshold, low dielectric constants and chemical stability [1,2], that could drive to important applications in non-linear optics and electrooptics.

Doping of KTP single crystals with different elements has been investigated in order to improve several properties like the ionic conductivity along the c direction [3–5], reduction of the KTP cut-off wavelength [6,7], etc. Recently, interests have shifted to the doping of KTP with lanthanide ions (Ln^{3+}) [7–11] for induction of second harmonic generation for fundamental wavelengths shorter

than 990 nm and the possibility of giving a self-doubled output. Attempts to dope KTP with Ln^{3+} have had a limited success, because of the low distribution coefficients of these ions in the KTP host [11]. The presence of codoping elements together with the rare earth doping generally increases the distribution coefficient of the Ln^{3+} . Codoping with Nb^{5+} is one of the most effective in this increasing [11]. Niobium has also been chosen as an ion for balancing the charge in the substitution of Ti^{4+} by Ln^{3+} and because of the favourable non-linear response it imparts in other solid-state oxides [12–14]. On the other hand completely substituting K^+ with Rb^+ clearly improves the distribution coefficient of Ln^{3+} [15,16]. In both cases, however, the Ln^{3+} concentration was still far below that needed for efficient fluorescence from the lanthanides and, therefore, for practical laser applications.

When these two strategies were merged, an Er^{3+} concentration of 0.65×10^{20} atoms cm^{-3} and a Yb^{3+} concentration of 1.95×10^{20} atoms cm^{-3}

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were obtained in a RTP:Nb crystal [17,18]. These concentrations are in the order of the ion concentration in other efficient laser materials.

The non-linear optical properties of RTP:Nb crystals also indicate a slight improvement in the generating power of the second harmonic signal for crystals grown in a solution containing around 4–5 mol% of Nb₂O₅ substituting TiO₂, to respect that of RTP [17,18]. Moreover, the efficiency of second harmonic generation does not decrease dramatically when Er³⁺ is present in the crystals [17,18].

In this paper we provide an overview of the possibilities for doping RTP:Nb with rare earth ions such as Er³⁺ and Yb³⁺ and study their spectroscopic and non-linear optical properties.

2. Crystal growth and structure determination

RTP, melts incongruently at 1443 K [19,20]. Single crystals cannot therefore be grown from the melt, at least under normal pressure. Hydrothermal techniques [21] and high-temperature solutions [22] have been reported to grow these crystals. During hydrothermal growth, however, OH⁻ groups are incorporated into the crystal lattice. To some extent this can be detrimental to the non-linear polarizability of RTP [23].

We grew RTP:(Nb,Ln) (Ln = Er and Yb) single crystals by high-temperature solution methods, using the top-seeded solution growth (TSSG)/slow-cooling technique. Details of this method have been reported previously [17,18,24,25].

Fig. 1 shows some of the RTP:(Nb,Ln) crystals we grew. We observed that when crystal seeds were

placed 5–10 mm from the centre of the surface of the solution, the average rate of growth of inclusion-free single crystals decreased as the concentration of niobium in the solution increased. Also, the differences between the dimensions in the *a* direction and the dimensions in the *b* and *c* directions were significant because the *a* dimension was smaller than the others. This difference in the dimension in *a* direction is produced by a change in the morphology of the crystals containing Nb [17,25]. To solve this problem, we designed a platinum stirrer immersed in the solution. We symmetrically fixed two crystal seeds around it at 1.5 cm from the centre of the surface of the solution and at 2 cm up from the turbine. This was to improve the mass transport conditions in the solution and minimise problems associated with non-homogeneous supersaturation [17]. With this system we obtained more inclusion-free single crystals, the quality of the crystals was higher and the differences in dimension between the *a*, *b* and *c* directions decreased. Stirring the solution also decreased the occurrence of spontaneous nucleation during the growth process [17,18,24,25]. However, the crystals were still not isometric, so we used crystal seeds of 5.0 mm in the *a* direction to try to increase the size of the crystal in this direction. Our results, although preliminary, show that this is a good way of obtaining isometric RTP:(Nb,Ln) crystals with typical dimensions of 5 × 5 × 5 mm in the *a* × *b* × *c* directions [26].

Some cracks normally appear in the crystal coming from the seed [17,18,24–26]. This problem may be due to the mismatch between the cell parameters of the seed and the cell parameters of the

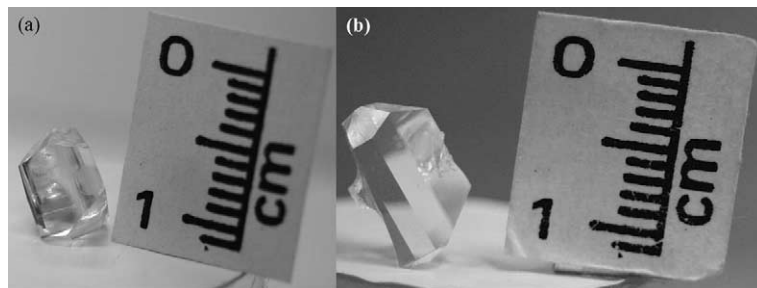


Fig. 1. Single crystals of (a) RTP:(Nb,Er) and (b) RTP:(Nb,Yb) grown by the TSSG technique.

crystal. This mismatch has been studied in the case of RTP:Nb and RTP crystals, however, the changes were small [17,27]. To get round these problems, several experiments were carried out using RTP and RTP:Nb seeds because with KTP:Nb crystals growth the problem was solved by using KTP:Nb seeds [28]. From our comparative studies, we concluded that the cracks in the RTP:(Nb,Ln) crystals appeared less often when RTP:Nb seeds were used, and some cracks-free crystals were obtained, but cracks could not be avoided completely.

We analyzed the concentration of Nb, Er and Yb in these crystals by EPMA. The concentrations of Er^{3+} and Yb^{3+} were the highest ever obtained in a crystal of the KTP family grown by flux methods (0.65×10^{20} and 1.95×10^{20} atoms cm^{-3} , respectively).

We determined the crystal structure of a $\text{RbTi}_{0.927}\text{Nb}_{0.056}\text{Er}_{0.017}\text{OPO}_4$ sample by neutron powder diffraction [29,30]. Nb and Er cations were only found to substitute Ti positions. From the two different crystallographic sites of Ti in the structure, Nb was only found in Ti(1) positions, while for Er, an undistinguishable situation to having Er equally distributed between Ti(1) and Ti(2) was observed. In this family of compounds, Ti(1) O_6 octahedra are slightly expanded than those of Ti(2) O_6 . As far as the ionic sizes of Ti^{4+} , Nb^{5+} and Er^{3+} are concerned, the tendency for Nb^{5+} ions to occupy Ti(1) sites (this does not happen with the more voluminous Er^{3+} cation) is not justified sterically and its origin is probably electrostatic [31].

3. Optical spectroscopy

3.1. RTP:(Nb,Er)

There is interest in Er^{3+} for applications in optical communications at long distances because of its efficient emission near the region of optical losses in silica fibres [32]. In medicine, one interest lies in its emission around 2.8 μm [33].

In the RTP:(Nb,Er) sample, 12 multiplets (${}^4\text{G}_{9/2}$, ${}^4\text{G}_{11/2}$, ${}^2\text{H}_{9/2}$, ${}^4\text{F}_{3/2}$, ${}^4\text{F}_{5/2}$, ${}^4\text{F}_{7/2}$, ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$, ${}^4\text{F}_{9/2}$, ${}^4\text{I}_{9/2}$, ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$) could be clearly

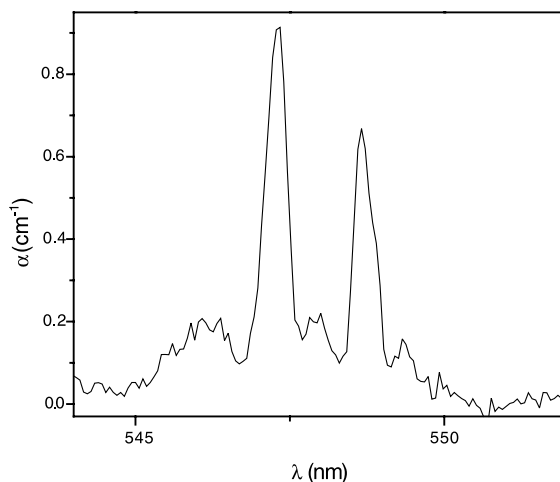


Fig. 2. ${}^4\text{S}_{3/2}$ optical absorption multiplet of Er^{3+} in RTP:(Nb,Er) at 6 K using incident polarized light parallel to the c crystallographic axis.

resolved at room temperature [24]. At 6 K we were also able to resolve the ${}^2\text{K}_{15/2}$ multiplet. These spectra were better defined than those of RTP:Er [15,16] because these crystals contained more Er^{3+} . The samples showed a strong dichroism [18,24,25].

At 6 K, we often found more optical absorption bands than we expected from multiplet splitting in the C_1 symmetry of titanium sites (see the absorption spectra for the ${}^4\text{S}_{3/2}$ multiplet in Fig. 2). This multiplet may be split by the crystal field into a maximum of two sublevels because of Kramers degeneracy of the odd electron configuration of Er^{3+} . However, Fig. 2 shows that at least five bands could be resolved. We believe this is associated with the coexistence of Ln in at least two different environments.

Fig. 3 shows the unpolarized room temperature ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ emission of Er^{3+} in RTP:(Nb,Er) crystals around 1550 nm after pumping at 521 nm. This is the most intense emission band we observed for Er^{3+} in these crystals.

3.2. RTP:(Nb,Yb)

Yb^{3+} is the most promising ion that can be used in a non-Nd laser in the same range of emission wavelength. It has several advantages over Nd^{3+} as a laser emitting center. Its energy level scheme,

compare this SHG efficiency with that of an RTP crystal containing only Nb at a similar concentration [17], we can clearly see this lower SHG efficiency. However, this decrease in efficiency was not dramatic in the level of dopants we studied. In fact, practically the same SHG efficiency as for pure RTP was achieved [17]. When the concentration of Nb is high in comparison to that of Ln, the non-linear optical response of the crystals is governed by the presence of Nb, and the SHG efficiency is high. Then, when the concentration of Ln increases in the crystals, the non-linear optical response decreases. This was confirmed because, for samples containing the same concentration of Ln but different amounts of Nb, the SHG efficiency of the sample containing the most Nb was the highest.

This reduction was previously attributed to a reabsorption of the green light generated by Er^{3+} in RTP:(Nb,Er) crystals, but we must now consider other factors because the simple energy level scheme of Yb^{3+} makes it impossible. As we showed in a previous study [29], the octahedral environment of TiO_6 is more symmetrical in crystals containing Nb and lanthanide ions than in crystals containing only Nb. We must therefore consider whether, as we suggested for KTP [16], the lanthanide ions occupy a more symmetrical position in the RTP structure. However, we can see that for similar concentrations of Er and Yb in the crystals, and with a similar concentration of Nb, the decrease in SHG efficiency in the sample containing Er is higher than in the sample containing Yb. This could be caused by the absorption of green light by Er^{3+} .

5. Conclusions and direction for future research

We successfully grew single crystals of RTP:(Nb,Er) and RTP:(Nb,Yb) of good optical quality. These were large enough to make later characterisations such as the spectroscopic studies of the Ln^{3+} ions in this matrix. A platinum turbine was used to stir the solutions. This improved the mass transport conditions in the solutions and so improved the quality of the crystals grown. Further improvements in the procedures for growing

crystals are needed to obtain high quality optical single crystals of RTP:(Nb,Ln) (Ln = Er and Yb). Using crystal seeds with the same composition as the crystals we would like to grow and with a larger dimension in the *a* crystallographic direction are promising directions for future research.

The resolution of the structure of the $\text{RbTi}_{0.927}\text{-Nb}_{0.056}\text{Er}_{0.017}\text{OPO}_4$ crystal confirmed that Nb and Er only go to Ti sites. However, further studies to determine more precisely the ionic environment of the Ln ions in RTP:Nb crystals are needed to know whether the Ti site environment has been modified by the Ln ions to form a quite symmetrical type of centre that may affect the crystal's non-linear optical properties. It would be also interesting to know whether the presence of Nb in the crystals helps to create a multiplicity of perturbed Ln centres.

Spectroscopic studies showed that there was a strong dichroism in the intensities of the different multiplets of Er^{3+} and Yb^{3+} that depended on the polarization of the incident light. Optical absorption and photoluminescence suggest that there are several Ln-related centres. Further studies are needed to determine the energy level schemes of these ions in the crystals and the role of the vibronic contribution in the relaxation of the different excited levels.

We found that the SHG efficiency of these crystals depended strongly on the ratio between the concentrations of Nb and Ln in the crystals. Further studies are needed to determine the non-linear optical coefficients of these crystals for their later application as laser crystals.

In conclusion, however, all of these observations show that a self-frequency doubling material can be obtained.

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References

- [1] M.E. Hagerman, K.R. Poeppelmeier, *Chem. Mater.* 7 (1995) 602.
- [2] M.N. Satyanarayan, A. Deepthy, H.L. Bhat, *Crit. Rev. Solid State Mater. Sci.* 24 (1999) 103.
- [3] T.F. MacGee, G.M. Blom, G.J. Kostecky, *J. Cryst. Growth* 109 (1991) 361.
- [4] R.J. Bolt, *J. Cryst. Growth* 126 (1993) 175.
- [5] T. Hörlin, R. Bolt, *Solid State Ionics* 78 (1995) 55.
- [6] L.T. Cheng, L.K. Cheng, R.L. Harlow, J.D. Bierlein, *Appl. Phys. Lett.* 64 (1994) 155.
- [7] M.T. Anderson, M.L.F. Phillips, G.D. Stucky, *J. Non-Cryst. Solids* 178 (1994) 120.
- [8] M.T. Anderson, M.L.F. Phillips, M.B. Sinclair, G.D. Stucky, *Chem. Mater.* 8 (1996) 248.
- [9] K.M. Wang, W. Wang, P.J. Ding, W.A. Lanford, Y.G. Liu, *J. Appl. Phys.* 77 (1995) 3581.
- [10] K.M. Wang, P.J. Ding, W. Wang, W.A. Landford, Y. Li, J.S. Li, Y.G. Liu, *Appl. Phys. Lett.* 64 (1994) 3101.
- [11] R. Solé, V. Nikolov, I. Koseva, P. Peshev, X. Ruiz, C. Zaldo, M.J. Martín, M. Aguiló, F. Díaz, *Chem. Mater.* 9 (1997) 2745.
- [12] S.K. Kurtz, T.T. Terry, *J. Appl. Phys.* 39 (1968) 3798.
- [13] A. Ashkin, G.D. Boyd, J.M. Dziedzic, R.G. Smith, A.A. Ballman, K. Nassau, *Appl. Phys. Lett.* 9 (1966) 72.
- [14] G.N. Van den Hoven, J.A. Van der Elsken, A. Polman, C. Van Dam, K.W. Van Uffelen, M.K. Smit, *Appl. Opt.* 36 (1997) 3338.
- [15] M. Rico, C. Zaldo, J. Massons, F. Díaz, *J. Phys.: Condens. Matter* 10 (1998) 10101.
- [16] C. Zaldo, M. Rico, F. Díaz, J.J. Carvajal, *Opt. Mater.* 13 (1999) 175.
- [17] J.J. Carvajal, V. Nikolov, R. Solé, Jna. Gavalda, J. Massons, M. Rico, C. Zaldo, M. Aguiló, F. Díaz, *Chem. Mater.* 12 (2000) 3171.
- [18] J.J. Carvajal, R. Solé, Jna. Gavalda, J. Massons, M. Rico, C. Zaldo, M. Aguiló, F. Díaz, *J. Alloys Compd.* 323–324 (2001) 231.
- [19] L.K. Cheng, J.D. Bierlein, A.A. Ballman, *J. Cryst. Growth* 110 (1991) 697.
- [20] V.I. Voronkova, V.K. Yanovskii, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 24 (1988) 273.
- [21] R.A. Laudise, W.A. Sunder, R.F. Belt, G. Gashurov, *J. Crystal Growth* 102 (1990) 427.
- [22] P.F. Bordui, J.C. Jacco, G.M. Loiacono, R.A. Stolzenberger, J.J. Zola, *J. Crystal Growth* 84 (1987) 403.
- [23] G. Hansson, H. Karlsson, S. Wang, F. Laurell, *Appl. Opt.* 39 (2000) 5058.
- [24] J.J. Carvajal, V. Nikolov, R. Solé, Jna. Gavalda, J. Massons, M. Aguiló, F. Díaz, *Chem. Mater.* 14 (2002) 3136.
- [25] J.J. Carvajal, R. Solé, Jna. Gavalda, J. Massons, M. Aguiló, F. Díaz, *Crystal Growth Des.* 1 (2001) 479.
- [26] J.J. Carvajal, R. Solé, Jna. Gavalda, J. Massons, M. Aguiló, F. Díaz, *Crystal Growth Des.*, submitted for publication.
- [27] J.J. Carvajal, R. Solé, Jna. Gavalda, J. Massons, F. Díaz, M. Aguiló, *Chem. Mater.*, submitted for publication.
- [28] J. Wang, Y. Liu, J. Wei, M. Jiang, Z. Shao, W. Liu, S. Jiang, *S. Cryst. Res. Technol.* 32 (1997) 319.
- [29] J.J. Carvajal, J.L. García-Muñoz, R. Solé, Jna. Gavalda, J. Massons, M. Aguiló, F. Díaz, *J. Solid State chem.*, in press.
- [30] J.J. Carvajal, J.L. García-Muñoz, R. Solé, Jna. Gavalda, J. Massons, X. Solans, F. Díaz and M. Aguiló, *Chem. Mater.*, submitted for publication.
- [31] P.A. Thomas, B.E. Watts, *Solid State Comm.* 73 (1990) 97.
- [32] G. Dominiak-Dzik, S. Golab, I. Pracka, W. Ryba-Romanowski, *Appl. Phys. A* 58 (1994) 551.
- [33] W. Koechner, *Solid-State Laser Engineering*, Springer Series in Optical Sciences, Springer-Verlag, Berlin, 1996, pp. 63–66.
- [34] P. Wang, P. Dekker, J.M. Dawes, J.A. Piper, Y. Liu, J. Wang, *Opt. Lett.* 25 (2000) 731.
- [35] V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikogosyan, *Handbook of Nonlinear Optical Materials*, Springer-Verlag, 1991.

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