

Chapter 3: **CRYSTALLISATION REGIONS OF RbTiOPO₄ CODOPED WITH Nb AND LANTHANIDE IONS**

Rubidium titanyl phosphate, RbTiOPO₄ (RTP), melts incongruently at 1443K^{161,174}. This means that decomposition occurs before melting, so single crystals cannot be grown from a melt, at least under normal pressure. For this reason, there are papers in the literature that report the application of the hydrothermal growth technique¹⁷⁵ and crystallisation from high-temperature solutions¹⁷⁶.

During hydrothermal growth, OH⁻ groups are incorporated into the crystal lattice of RTP. This results in a sharp absorption peak at 2.7-2.8 μm in the transmission spectrum of these crystals. According to some authors¹⁷⁷, the OH⁻ impurity can, to some extent, be detrimental to the non-linear polarisability of RTP, as with potassium titanyl phosphate, KTiOPO₄ (KTP).¹⁷⁸

In the crystal growth from high-temperature solutions, or flux growth, the components of the crystal to be grown are dissolved in a solvent, known as a flux. The main advantage of flux growth is that the crystals are grown below their melting temperature, so the method can be used to grow

materials that melt incongruently. The free growth into a liquid allows the formation of growth facets. The growth rates differ for the growth directions of the various facets, which could lead to inhomogeneities in the crystal. Flux inclusions are also often observed. However, these problems can be avoided and in this thesis we have grown high quality RTP crystals by flux growth.

When using high-temperature solution growth techniques to prepare high-quality crystals whose sizes are suitable for practical purposes, it is very important to find an appropriate solvent, to know how this solvent interacts with the dissolved substance and to know the properties of the solutions obtained. If we know these factors, we can choose the best growth regimes.¹⁷⁹

Most studies on the growth of RTP single crystals use solutions of the Rb₂O-P₂O₅-TiO₂ system.^{174,180-182} This flux is very viscous. In fact, it is as viscous as the flux in the crystal growth of KTP.^{183,184} The viscosity can be halved by adding tungsten oxide to the solution.¹⁸⁵ Therefore, adding, for example, tungstate, lead fluoride and molybdate lowers the viscosity and volatility of the fluxes of the RTP isomorphous crystals and enables faster growth at lower temperatures.¹⁶¹ Unfortunately, impurities are then incorporated into the crystal. For example, tungsten impurities are incorporated at the two titanium sites.¹²⁴ The use of a self-flux, where only the constituents of the crystals are present, is therefore recommended.¹⁸⁶ This prevents the incorporation of other elements and lowers the impurity content.

Until the publication of our study on the crystallisation region of the RTP phase (see [paper V](#)), there were no data available about the concentration region and temperatures of RTP crystallisation.

The aim of this section is to study the Rb₂O-P₂O₅-TiO₂ system in order to determine the crystallisation region and the crystallisation temperatures of the RbTiOPO₄ phase in this system. We have also studied how the crystallisation region changes when WO₃ is incorporated into this system. Crystals of RTP grown in a flux containing tungsten oxide are also interesting for applications that do not require much power. These crystals grow faster than RTP crystals grown in a self-flux because the solution is less viscous, so they can be cheaper. Finally, as our main objective is to obtain RTP crystals codoped with Nb⁵⁺ and Ln³⁺, we studied how the crystallisation region of RTP changes when Nb₂O₅ and Ln₂O₃ are introduced into the solution.

3.1. The crystallisation region of RbTiOPO₄ in self-flux and in fluxes containing WO₃.

To determine the concentration region and crystallisation temperatures of the RbTiOPO₄ phase in the self-flux and in fluxes containing WO₃, we investigated 30-40 different solution compositions in the Rb₂O-P₂O₅-TiO₂ and Rb₂O-P₂O₅-TiO₂-WO₃ systems. The crystallised phase was identified by X-ray diffraction analysis and electron probe microanalysis (EPMA), and the shape of the crystals was

observed by optical and electron microscopies. We measured the saturation temperature of the solution (T_s) more accurately by observing the growth or dissolution of an RTP seed when it came into contact with the solution surface.

Figure 2 in [paper V](#) shows the crystallisation region of RTP in self-flux and the saturation temperature isotherms. In [paper V](#) we also studied how the crystallisation region of RTP changed when WO₃ was introduced into the solution. Figures 3-5 in [paper V](#) show the crystallisation regions of RTP in solutions containing 10, 20 and 30 mol % WO₃, respectively. These figures also show the saturation temperature isotherms.

If we compare the RTP crystallisation region in the Rb₂O-P₂O₅-TiO₂ system with the region when WO₃ was present in the solutions, we can see that there was a displacement to Rb₂O-rich regions when the concentration of WO₃ increased. The RTP crystallisation region with 30 mol % WO₃ in the solution was significantly narrower than the regions obtained with lower WO₃ contents. For solutions with a higher mol % of WO₃, this region is expected to disappear.

In all cases, the saturation temperature isotherms were parallel to the RTP crystallisation boundary in the Rb₂O-rich region. The T_s slightly decreased when the concentration of WO₃ increased, especially to above 20 mol %.

The neighbouring phases identified in this case were TiO₂ (rutile) in the region that was poor in P₂O₅ and rich in TiO₂, and Rb₃Ti₃O(P₂O₇)(PO₄)₃ in the region that was rich in P₂O₅ and poor in Rb₂O. Highly hygroscopic and water-soluble phases appeared in the region that was poor in TiO₂ and rich in Rb₂O. Because of their hygroscopic nature, these phases are still unidentified. When there was enough WO₃ in the solution, a new neighbouring phase appeared in the region that was poor in Rb₂O. This was identified as RbTiPO₅:W. For solution concentrations of WO₃ above 30 mol %, the Rb₃Ti₃O(P₂O₇)(PO₄)₃ phase disappeared and only the RbTiPO₅ phase was found. The morphology of Rb₃Ti₃O(P₂O₇)(PO₄)₃ in solutions with WO₃ is different from its morphology in without WO₃. In solutions without WO₃, transparent crystalline colourless prisms appear, and in solutions with WO₃, the phase grows as opaque violet crystalline thin plates.

3.2. Changes in the crystallisation region of RbTiOPO₄ when Nb₂O₅ and Ln₂O₃ are introduced into the solution.

We chose two basic molar ratios of Rb₂O-P₂O₅-TiO₂ to study how the crystallisation region of RTP and the distribution coefficients of dopants vary when TiO₂ is substituted by Nb₂O₅ and Ln₂O₃ in the solution (see [paper VI](#)). These molar ratios were Rb₂O-P₂O₅-TiO₂ = 43.1-31.9-25.0 and 40.8-27.2-32.0.

Figures 1-4 in [paper VI](#) show how the crystallisation region of RTP changed when some of the TiO₂ in the solution was substituted by Nb₂O₅ and Er₂O₃ or Nb₂O₅ and Yb₂O₃. The critical concentration of the dopants that substituted TiO₂ in solution, below which the RTP phase crystallised and above which other phases appeared, are very important parameters for growing RTP:(Nb,Ln) crystals. As the solution was poorer in Rb₂O and P₂O₅ and richer in TiO₂, the critical concentration of Nb decreased, whereas the critical concentration of Ln increased. If we compare the two Ln, we can see that when the solution composition was equal and the solution was poor in TiO₂, the critical concentration of Er₂O₃ was higher than that of Yb₂O₃. However, when the concentration of TiO₂ in the initial solution was richer, the critical concentration of Er₂O₃ was lower than that of Yb₂O₃. We have identified several new phases in the boundary of the RTP crystallisation regions in these systems. When the critical concentration of Nb₂O₅ was surpassed, RbTiPO₅:Nb phase was observed. In solutions whose TiO₂ content was low, we identified Rb₂Ti_{2-x}Ln_x(PO₄)₃ when the critical concentration of Ln₂O₃ was surpassed. In solutions whose TiO₂ content was high, the neighbouring phases of the crystallisation region of RTP depended on the Ln used. When the critical concentration of Er₂O₃ was surpassed, we detected ErPO₄ and when the critical concentration of Yb₂O₃ was surpassed, we identified Rb₃Yb₂(PO₄)₃.

The most significant differences were in the distribution coefficients of these ions in the crystallisation regions we studied. These distribution coefficients are listed in Tables 1-4 in [paper VI](#). The distribution coefficient of Ln increased as the concentration of Nb₂O₅ increased up to a maximum of around 2-6 mol % and depended on the composition of the initial solution and the Ln studied. The distribution coefficient then decreased. This may have been due to a competition mechanism between the Ln and Nb ions, because both Ln and Nb substitute Ti in the structure (see Chapter 4). Therefore, as the Nb ion is smaller than the Ln ion, the mobility of Nb is higher. Also, because its radius is closer to that of Ti⁴⁺, the probability that this ion occupies the positions of Ti is greater. This mechanism is confirmed by the fact that when the concentration of Nb in the solution increases, its distribution coefficient in the crystal decreases because, as Nb cannot totally substitute Ti in the structure there are not enough free places that can be occupied by Nb.

The fact that the distribution coefficients of Yb were higher than those of Er (see Tables 1 and 3 or Tables 2 and 4 in [paper VI](#)) may be due to the ionic radii. As Ln substitutes Ti⁴⁺ in the structure, the ion whose ionic radius is closer to that of Ti⁴⁺ have a greater tendency to incorporate into the crystals and therefore have larger distribution coefficients. To explain the higher distribution coefficient of Ln in initial solutions containing a higher concentration of TiO₂ and a higher Rb₂O/P₂O₅ ratio (see Tables 1-4 in [paper VI](#)), we assumed that the viscosity of the solution was higher when the Rb₂O/P₂O₅ ratio decreased, bearing in mind that a similar behaviour was observed in self-flux solutions of KTP.¹⁸⁵ Therefore, if the solution is more viscous, the mobility of the ions is more difficult and they tend to be

less incorporated into the crystal. The high viscosity of the solution works against its homogeneity, producing a lack of mixing and it is difficult for the Ln to form structural units that can be incorporated into the crystal. However, other parameters, such as the saturation temperature, which is higher for solutions containing more TiO₂, may also be responsible for this effect. At higher temperatures, the structure is more expanded and Ln can enter the structure more easily. Other parameters that may be responsible are the speed at which crystals grow, the diffusion coefficient and how far the growth conditions are from the equilibrium thermodynamic conditions.

The distribution coefficients of Nb were higher than those of Ln because its ionic radius is closer to that of Ti⁴⁺.¹⁸⁷ We found that, due to saturation, K_{Nb} decreased as the concentration of Nb₂O₅ increased. We also found that there was a reciprocal action of Nb on the Ln ions: the presence of Nb in the crystals improved the distribution coefficient of Ln and, though to a lesser extent, the Ln also improved the distribution coefficient of Nb in the crystals.

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