Nonlinear optical properties of the flux grown RbTiOPO$_4$ crystal

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Abstract

Refractive indices of flux grown RbTiOPO$_4$ (RTP) were measured in the wavelength interval 0.406 to 1.064 μm and Sellmeier equation coefficients were calculated. Phase-matching curves for second harmonic generation from radiation with wavelengths of 1.064 μm and 1.079 μm were obtained. RTP nonlinear optical properties are compared to those of KTP. Second-harmonic generation in RTP crystal is carried out with the efficiency of 65%.

1. Introduction

Potassium titanyl phosphate KTiOPO$_4$ (KTP) is a well-studied and widely used nonlinear optical crystal [1–6]. Some of the materials, isostructural to KTP, have also demonstrated nonlinear optical properties [2,7,8]. Rubidium titanyl phosphate RbTiOPO$_4$ (RTP), being the most famous of them, was first obtained by hydrothermal method [1], and then by the flux-growth method [2]. RTP flux growth has some problems due to the appearance of two isomorphic crystalline phases, one of them being identical to KTP, and the other phase has a cubic structure and does not demonstrate nonlinear optical properties [9].

The nonlinear optical properties of RTP are similar to KTP and in some cases the application of RTP instead of KTP may be preferable, but detailed information on the optical properties of RTP is required. The investigations of nonlinear waveguide devices based on a KTP–RTP pair [10,11] also should be mentioned, as the fabrication of these waveguides requires the knowledge of RTP refractive indices as well.

Thus, the accurate determination of RTP refractive indices and calculation of the Sellmeier coefficients are necessary for the successful application of this material in nonlinear optical devices. Nevertheless, it has not been done so far. The accuracy of the data listed in Ref. [1] is insufficient, and in Refs. [12,13] the measurements were carried out in a very narrow spectral band, which gives no possibility of precise determination of the Sellmeier coefficients.

The accurate measurement of RTP refractive indices in a wavelength interval of 0.406 to 1.064 μm and the fitted values of the Sellmeier coefficients are presented in this paper. Furthermore, the phase-matching curve, effective nonlinear coefficient and walk-off angle curves are obtained for λ = 1.064 μm (Nd: YAG laser) and λ = 1.079 μm (Nd: YAP laser). Optical damage threshold, angle and temperature phase-matching bandwidth of RTP were also determined. All the data are listed in comparison with KTP.

2. Refractive indices and Sellmeier equation

The RTP crystal was obtained by the flux growth method in the phosphate system. The growth process...
is described in detail in Ref. [9]. Typical dimensions of the bulk crystals obtained were $30 \times 40 \times 60$ mm$^3$ enabling us to fabricate frequency converters up to $10 \times 10 \times 10$ mm$^3$ from uniform, inclusion free regions of the crystal. The uniformity of the crystal structure was testified by the uniformity of the radiation conversion into the second harmonic in a wide beam all over the converter section.

Two prisms with an angle of about $30^\circ$ and the facet of 1.0 cm$^2$ were fabricated in order to measure the refractive indices. Every prism was oriented so that in the position of minimal deviation the beam was propagated along one of the crystal axes ($X$-axis for the prism 1 and $Y$-axis for the prism 2). The measurements were carried out on a goniometer, the tolerance of the minimal deviation angle was less than 10 s of arc, and of the prism angle was less than 5 s of arc. This ensured the determination of the refractive indices with an accuracy of $2 \times 10^{-4}$. Experimental results corrected with the refractive index of air are listed in the Table 1 together with the values of the refractive indices calculated from a Sellmeier equation of the form

$$n^2(\lambda) = A + \frac{B}{1 - C\lambda^{-2} - D\lambda^2}, \quad (1)$$

where $\lambda$ is the vacuum wavelength measured in $\mu$m.

The fit of the coefficients $A$, $B$, $C$ and $D$ was performed by a least-squares routine, the results are given in Table 2.

<table>
<thead>
<tr>
<th>$\lambda$, $\mu$m</th>
<th>$n_X$</th>
<th></th>
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### 3. Phase-matching curves

Calculating the refractive indices via the Sellmeier equation (1), we can obtain the phase-matching angles of RTP. Here we consider the process of the second harmonic generation (SHG) with incident wavelengths of 1.064 $\mu$m and 1.079 $\mu$m. The results of calculation of the type II phase-matching curves $\theta(\phi)$ in KTP and RTP are shown in Fig. 1 (type-I phase-matching should not be used for frequency doubling at $\lambda > 1.0$ $\mu$m because of small value of the effective nonlinear coefficient).

We have also measured the angles of type II phase-matching in the principal planes of RTP crystal, the experimental results are listed in Table 3 together with the calculated values. Taking into account that the experimental values were measured with a tolerance of about 0.5° and the calculated values are extremely sensitive to the accuracy of the refractive indices fit, the coincidence of these phase-matching data is quite satisfactory.

It should be noted that our values of RTP refractive indices differ significantly from the results given in Refs. [12–14] (the difference amounts to $5 \times 10^{-3}$ at some wavelengths). As a result, the values of the Sellmeier coefficients listed in Table 1, differ from the values given in Ref. [14]. This discrepancy couldn’t be explained by the influence of any chemical admixture, as our X-ray diffraction data [5] coincide with those of Ref. [12]. Note, however, that the phase-matching angles of RTP calculated from our
Table 2

Sellmeier equation coefficients of RTP

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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Table 3

Phase-matching angles of RTP in the principal planes

<table>
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<th>λ, μm</th>
<th>XY plane (θ = 90°)</th>
<th>YZ plane (φ = 90°)</th>
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<td>58.0</td>
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<td>1.079</td>
<td>48.5</td>
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</table>

set of the Sellmeier coefficients, are in good agreement with experimental data (see Table 3).

The values of the RTP phase-matching angles listed in Ref. [1] at the wavelength of $\lambda = 1.064 \mu m$ also differ from our data at about 5°. This is probably caused by the difference in the refractive indices of RTP crystals grown by hydrothermal and by flux growth methods.

To determine the effective nonlinear coefficient $d_{eff}$, let us take into account that the values of the nonlinear coefficients $d_{ij}$ of KTP and RTP are equal [1]. This can be explained by the fact that the $d_{ij}$ values are defined mainly by the asymmetrical distribution of the charge in Ti-O chains and do not depend upon the radius of the alkaline metal ion [7]. The values of the nonlinear-optical coefficients of KTP are given in Ref. [15] (at $\lambda = 1.064 \mu m$):

- $d_{31} = 2.54 \text{ pm/V}$
- $d_{32} = 4.35 \text{ pm/V}$
- $d_{33} = 16.9 \text{ pm/V}$
- $d_{24} = 3.64 \text{ pm/V}$
- $d_{15} = 1.91 \text{ pm/V}$

Since the approximate formula for the calculation of $d_{eff}$ from Ref. [6] gives an error of about 20%, it is preferable to calculate this value immediately:

$$d_{eff} = b_{30}^2 d_{33} b_{30}^2 b_{30},$$

where $b_{30}^2$, $b_{30}$ and $b_{30}$ are the polarization vectors of the wave with frequency $2\omega$ and of two perpendicular waves with frequencies $\omega_i$, respectively. The expression for $d_{eff}$ was found to be very cumbersome. Fig. 2 shows $d_{eff}$ as a function of $\phi$ for the type II phase-matching. The values of $d_{eff}$ for the type I phase-matching was proved to be significantly smaller limiting the use of this type of phase-matching for RTP.

It should be stressed that the difference in the values of $d_{eff}$ for RTP and KTP is caused only by the difference of the phase-matching angles. To check this, we have measured the ratio of these values at $\lambda = 1.064 \mu m$ in the $XY$ plane. As the conversion efficiency depends essentially on the quality of the crystal, the accuracy of these measurements was not high. Averaging the measurement of the conversion efficiency of several KTP and RTP crystals of the best quality, we have obtained that this ratio is $0.75 \pm 0.05$, in good agreement with the calculated value: $d_{eff}(\text{RTP}) / d_{eff}(\text{KTP}) = 0.732$. Note that the values of the nonlinear-optical coefficients of KTP reported earlier in
The input and output faces were antireflection coated from inclusion-free regions of RTP crystal [9]. We have used a Q-switched Nd:YAG laser working at TEM\textsubscript{00} mode with a pulse duration of 15 ns and a pulse repetition rate of 10 Hz. The incident beam was of uniform intensity distribution across the beam section. The conversion efficiency as a function of the incident power density for a crystal 6.9 mm long is shown in Fig. 3. Thus, the conversion efficiency in a RTP crystal of good quality reached 65%.

A damage of the input surface was observed when the incident power density reached 900 MW/cm\textsuperscript{2}. However, this value couldn't be compared immediately with previously known results for KTP, because the optical damage threshold value depends on the laser beam parameters, beam propagation direction, the quality of crystal surface polishing, etc. To compare the optical damage threshold values of RTP and KTP, we have measured them under the same conditions. Both crystals, KTP and RTP, were grown by the flux growth method from pure phosphate system.

It was proved in this experiment, that the optical damage threshold of RTP is essentially larger than that of KTP. The ratio of these values measured under the same laser beam parameters, is

\[
\frac{I(\text{RTP})}{I(\text{KTP})} = 1.8 \pm 0.2 .
\] (3)

Ref [11] differ significantly from those of Ref [15], giving essentially a greater value of the ratio of the effective nonlinear coefficients (about 0.9).

The walk-off angles for the type II SGH are also calculated in KTP and RTP at \(\lambda = 1.064\) and 1.079 \(\mu\)m wavelengths (Fig. 2). The walk-off angle was defined as the largest angle between the Poynting vectors of the incident and second-harmonic waves. An analysis of the curves represented in Figs. 1, 2 shows that the type II phase-matching in the \(XY\) plane is optimum for second harmonic generation in the RTP crystal, the phase-matching angle being \(\phi = 58.8^\circ\) at \(\lambda = 1.064\) \(\mu\)m and \(\phi = 48.5^\circ\) at \(\lambda = 1.079\) \(\mu\)m. The value of \(d_{\text{eff}}\) for RTP is somewhat smaller than that for KTP, and the walk-off angle is somewhat greater.

### 4. Second harmonic generation

The investigation of the second harmonic generation process was performed with converters fabricated from inclusion-free regions of RTP crystal [9]. The input and output faces were antireflection coated for \(\lambda = 1.064\) \(\mu\)m and \(\lambda = 0.532\) \(\mu\)m, respectively. We have used a Q-switched Nd:YAG laser working at TEM\textsubscript{00} mode with a pulse duration of 15 ns and a pulse repetition rate of 10 Hz. The incident beam was of uniform intensity distribution across the beam section. The conversion efficiency as a function of the incident power density for a crystal 6.9 mm long is shown in Fig. 3. Thus, the conversion efficiency in a RTP crystal of good quality reached 65%.

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\frac{I(\text{RTP})}{I(\text{KTP})} = 1.8 \pm 0.2 .
\] (3)

The phase-matching angle bandwidth in the critical direction in the \(XY\) plane can be calculated on the basis of the measured refractive indices (see Ref. [4]):

\[
\Delta \phi = \left. \frac{2\pi n_{\text{eff}}}{\partial \Delta k / \partial \phi} \right|_{\phi = 0} .
\] (4)

![Fig. 3. Conversion efficiency as a function of incident power density for the 6.9 mm long RTP crystal.](image-url)
where $l$ is the crystal length, $n_{\text{eff}} = \left[ n_{2\omega}(\phi) + n_{\omega, z} \right] / 2$, and $\Delta k = k_{2\omega}(\phi) - k_{\omega}(\phi) - k_{\omega, z}$ is the difference of the wave vectors for the waves with frequencies $2\omega$ and $\omega$ (with the appropriate polarization). The factor $x = 1.39$ takes into account that the angle bandwidth is measured at half intensity level.

Calculating the derivative

$$\frac{\partial \Delta k}{\partial \phi} = \frac{\partial}{\partial \phi} k_{2\omega}(\phi) - \frac{\partial}{\partial \phi} k_{\omega}(\phi)$$

$$= \frac{2\pi}{\lambda} \left( 2 \frac{\partial}{\partial \phi} n_{2\omega}(\phi) - \frac{\partial}{\partial \phi} n_{\omega}(\phi) \right)$$

with the help of Fresnel equation for the refractive index written at $\theta = 90^\circ$: $1/n^2 = 1/n_3^2 + 1/n_\omega^2$, and substituting the numerical values, we obtain:

$$\Delta \phi l = 12 \text{ mrad cm}. \quad (6)$$

For a converter 5.6 mm long the intensity of the second harmonic generation was observed to reduce by a factor of 2 when the angle is changed at $2.3^\circ$ from the phase-matching direction. So the experimental value of the angle phase-matching bandwidth for RTP crystal determined at half intensity level is $(\Delta \phi l)_{\text{exp}} = 13.2 \text{ mrad cm}$, being in good agreement with the calculated value. For KTP this value equals 13 mrad cm [5,6]. Thus, the measured angle phase-matching bandwidth of the RTP crystal coincides with that of KTP.

To measure the temperature phase-matching bandwidth of RTP the converter was turned at a small angle $\Delta \phi$ from the phase-matching position. Then it was heated slowly and the efficiency of the second harmonic generation was measured. A typical phase-matching curve for a crystal 12.4 mm long is shown in Fig. 4. These measurements were performed with several converters of good uniformity under different values of $\Delta \phi$. It was proved that the width of the phase-matching curve shown in Fig. 4 does not depend on the angle shift $\Delta \phi$. The resulting value of the temperature phase-matching bandwidth of RTP measured at half intensity level, is

$$\Delta T l = 40^\circ\text{C cm}. \quad (7)$$

This value is essentially higher than the temperature phase-matching bandwidth of KTP ($25^\circ\text{C cm}$) [5,6].

Fig. 4. Temperature phase-matching curve for 12.4 mm long RTP crystal.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>RTP and KTP nonlinear optical properties for the process of second harmonic generation at $\lambda = 1.064 \mu\text{m}$ (type II phase-matching in the $XY$ plane)</th>
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<tbody>
<tr>
<td>KTP</td>
<td>RTP</td>
</tr>
<tr>
<td>Phase-matching angle, deg</td>
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<tr>
<td>Effective nonlinear coefficient, $10^{-12} \text{ m/V}$</td>
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<tr>
<td>Walk-off angle, deg</td>
<td>0.26 0.40</td>
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<tr>
<td>Angle phase-matching bandwidth, mrad cm</td>
<td>13 13</td>
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<td>Temperature phase-matching bandwidth, °C cm</td>
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<td>Optical damage threshold ratio $I(\text{RTP})/I(\text{KTP})$</td>
<td>– 1.8</td>
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5. Conclusions

In this paper the results of the measurements of RTP refractive indices are represented and Sellmeier coefficients are calculated. Type II phase-matching angles, effective nonlinear coefficients and walk-off angles are calculated for second harmonic generation at the wavelengths of 1.064 $\mu\text{m}$ and 1.079 $\mu\text{m}$. The calculated results are in good agreement with the experimental data. The optical damage threshold, angle and temperature phase-matching bandwidths were also measured. In Table 4 the nonlinear optical characteristics of RTP are compared with those of KTP. The data on KTP corresponds to a crystal grown by the flux growth method from pure phosphate system.

These data demonstrate that RTP and KTP crystals have similar nonlinear optical properties, but some parameters of RTP exceed those of KTP. In
particular higher optical damage threshold and wider temperature phase-matching bandwidth should be stressed, which makes preferable to use RTP for conversion in the quasi-continuous regime under a high average radiation power [16].

Acknowledgements

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References