Article

Terahertz Optical Properties of KTiOPO4 Crystal in the Temperature Range of (−192)–150 °C

Alina Rybak 1,2, Valery Antsygin 2, Alexander Mamrashev 2, and Nazar Nikolaev 2,*

1 Laboratory of Functional Diagnostics of Low-Dimensional Structures for Nanoelectronics, Novosibirsk State University, 630090 Novosibirsk, Russia; a.rybak1@g.nsu.ru
2 Terahertz Photonics Group, Institute of Automation and Electrometry SB RAS, 630090 Novosibirsk, Russia; antsygin@iae.nsk.su (V.A.); mamrashev@iae.nsk.su (A.M.)
* Correspondence: nazar@iae.nsk.su

Abstract: This paper presents the results of an experimental study of the optical properties of highly resistive monocrystals of potassium titanyl phosphate (KTiOPO4, KTP) in the frequency range of 0.2–1 THz and the temperature range of (−192)–150 °C. The dispersion of the refractive indices is approximated in the form of Sellmeier equations. The results show that the temperature dependence of the Sellmeier coefficients for all three principal optical axes is close to linear and, most likely, does not experience an extremum in the vicinity of the activation temperatures of the cationic conductivity of the KTP crystal at (−73)–(−23) °C. Weak frequency dependence of an optical axis direction angle $V_Z$ in the range of 0.2–1 THz is confirmed. However, the change in $V_Z$ with temperature is three times higher than reported before.

Keywords: potassium titanyl phosphate; KTiOPO4; terahertz spectroscopy; dispersion; refractive index; Sellmeier equations; temperature dependence

1. Introduction

Potassium titanyl phosphate crystal (KTiOPO4, KTP) is a well-known nonlinear optical material for efficient frequency conversion of laser radiation in the near- and mid-infrared range. The popularity of KTP originates in its high laser-induced damage threshold of up to 30 GW/cm² (single-shot measurement with 8.5 ns pulses at the wavelength of 1.064 µm [1]), wide transparency range of 0.35–4.5 µm, sufficiently high nonlinear optical coefficients of $d_{31} = 2.2$ pm/V, $d_{32} = 3.7$ pm/V and $d_{33} = 14.6$ pm/V [2], and possibilities of manufacturing periodically poled structures in the crystal.

Presently, KTP is considered a promising material for converting infrared (IR) laser radiation to terahertz waves [3–8]. It is important for the development of small-size terahertz (THz) radiation sources tunable in a wide frequency range and possessing high spectral brightness. Among the tasks that could be solved with the help of such sources one should notice gas analysis, in particular, the construction of a terahertz Light Detection and Ranging (LiDAR) for monitoring minor gas components in the ground layer of the atmosphere on kilometer-length paths for the environment and climate control [9,10]; investigation of nuclear spin isomers of molecules and their conversion [11,12]; development of compact accelerators for charged particles [13]; the advancement of nonlinear optics to new spectral ranges [14] and study of selective effects of THz radiation on living organisms [15].

In several works, the terahertz optical properties of KTP crystals were studied in detail, and the collinear phase-matching conditions for the terahertz difference frequency generation (DFG) under IR laser pumping were calculated [3–6]. Numerical simulations presented in [4] also confirm the possibility of frequency conversion within the terahertz range. The possibility of generating THz waves by stimulated polariton scattering (SPS) was experimentally demonstrated by the group of Prof. Yen-Chieh Huang [7,8]. In this...
case, due to the higher laser-induced damage threshold, KTP was shown to be a more efficient converter than lithium niobate [8].

It was demonstrated recently that cooling the KTP crystals to liquid nitrogen temperature significantly decreases their terahertz absorption coefficient [3,4]. This should increase the efficiency of the KTP crystal in THz photonics applications. Along with this, thermoelectric measurements demonstrated that the electrical conductivity mechanism of KTP crystals along the c-axis also changes its character with cooling. It was shown in [16,17] that at temperatures below −73 °C, electrons are the predominant charge carriers. In the temperature range of (−73)−(−23) °C, the conductivity is bipolar, and at T > −23 °C, cationic conductivity is dominant. The exact temperature values can vary due to crystal quality and doping. The observed change in the dielectric response of the crystal with temperature is determined by the gradual freezing of the motion of the K⁺ ions. This can potentially lead to an abrupt change in the terahertz dielectric response since it is mainly determined by phonon modes below 6 THz which are associated with vibrations of the potassium sublattice of the crystal [18]. An abrupt change in the dielectric response can potentially influence the efficiency of nonlinear THz-wave generation.

Previously, KTP crystals were investigated only at room and liquid nitrogen temperatures. For a full characterization of the KTP crystal, it is also important to study in detail its terahertz optical properties at intermediate temperatures. This is the goal of the present work in which we comprehensively investigate KTP terahertz optical properties in the temperature range from −192 °C to +150 °C using terahertz time-domain spectroscopy. To increase measurement accuracy in the subterahertz range, samples with a thickness of about 3 mm were studied. The results are presented in the frequency range of 0.2−1 THz limited by the absorption of the thick samples and the dynamic range of the spectrometer.

2. Materials and Methods

Two a- and b-cut samples with the dimensions of 9 × 9 × 3 mm³ were fabricated from KTP crystals. The crystals were grown by the Czochralski method and supplied by Castech Inc. (Fujian, China). Large facets were polished to high optical quality. The measured direct current conductivity of the samples along the c-axis was ~10⁻¹⁰ Ohm⁻¹·cm⁻¹ at room temperature. As in previous works [2–4], the following correspondence between the optical and crystallographic axes was accepted: x, y, z → a, b, c.

The measurements were carried out using a conventional terahertz time-domain spectrometer developed at the Institute of Automation and Electrometry SB RAS (Figure 1). The spectrometer is based on the radiation of the second harmonic of a femtosecond Er-fiber laser (Toptica Photonics AG, Munich, Germany, λ = 775 nm, τ = 130 fs, P = 100 mW). An interdigitated photoconductive antenna (Batop GmbH, Jena, Germany) is used to generate THz radiation. Detection is carried out by the free-space electro-optic sampling technique in a 2-mm-thick ZnTe crystal [19,20]. The spectral range of the system is 0.2−2.5 THz; the dynamic range is more than 70 dB at the frequency of 0.3 THz. THz signals are acquired with a time step of 125 fs in the 60 ps range which corresponds to the spectral resolution of ~20 GHz. Statistical errors of the measured parameters are determined from four experimental sets. Metal grid polarizers are used to increase the polarization contrast of the system. Before the measurement, samples are positioned so that the linear polarization of the THz wave is parallel to the principal optical axis under study. Processing of terahertz signals and calculation of the optical properties of samples were carried using the algorithm from [21].
A nitrogen bath cryostat with fused silica windows was used in the study. The cryostat was equipped with a resistive heater attached to a neck of a copper sample holder. This custom-made sample holder had two identical holes with a diameter of 7 mm in its lower flat part (Figure 1). One hole accommodated samples under investigation; the other was used to record reference THz signals by moving the entire cryostat by a motorized linear translation stage (Newport, RI, USA) perpendicular to the THz beam. The temperature was measured using a chromel-alumel thermocouple fixed near the sample. The temperature was stabilized with an accuracy of ±0.5 °C using a computer-controlled thermal regulator TRM251 (Oven, Moscow, Russia).

3. Results

Spectral dependences of KTP absorption coefficients at the temperatures of −192 °C; −150 °C; −100 °C; −50 °C; 25 °C; 50 °C; 100 °C and 150 °C are shown in Figure 2. Absorption coefficients increase as the radiation frequency increases, which is associated with the presence of phonon modes above 1 THz. As shown earlier in [3], the absorption maxima of phonon modes for $\alpha_x$ at room temperature are near 1.75 THz and 2.2 THz; for $\alpha_y$, near 2.15 THz; and for $\alpha_x$, near 2.44 THz. At 25 °C the values of the absorption coefficient $\alpha_x$ in the range of 0.5–1 THz increase from 5 cm$^{-1}$ to 15 cm$^{-1}$, while the other two absorption coefficients are close to each other, $\alpha_x \approx \alpha_y$, and they are approximately five times smaller than $\alpha_{2x}$, which is in good agreement with the previous measurements [3,4].

Note that in [3,4], a weak broad absorption peak with a maximum of ~30 cm$^{-1}$ in the vicinity of 0.9 THz ($\lambda = 333 \mu$m) was detected in the $\alpha_2$ spectrum. This peak is absent in our case at all temperatures. Perhaps this indicates a better quality of the KTP crystals studied in the present work. Previously observed absorption peak can be associated with the wavevector selection rule breakdown due to defect-induced disorder. As a result, the manifestation of acoustic phonon oscillation can be seen in the low-frequency absorption spectrum. A similar effect was observed in LiNbO$_3$ crystal using Raman spectroscopy [22]. In the work of Mounaix et al. [23], the spectral resolution and spectral range did not allow unambiguous detection of the peak; however, the absorption coefficient
of the slow axis at 1 THz had a value close to 20 cm\(^{-1}\) that corresponds to our present result. Figure 2a,b demonstrate that the values of \(\alpha_x\) and \(\alpha_y\) are below 5 cm\(^{-1}\) at frequencies \(\leq0.75\) THz at all temperatures. Upon cooling to \(-192\) °C, the absorption along all axes decreases to the values <1 cm\(^{-1}\).

The temperature dependencies of the KTP refractive index spectra are presented in Figure 3. The data demonstrate an increase in the refractive index with increasing frequency. This is also due to the crystal phonon modes above 1 THz. These results are in good agreement with the data obtained at room temperature and liquid nitrogen temperature in the previous works. The refractive indices at 1 THz are \(n_x = 4.00\), \(n_y = 3.35\), and the birefringence at room temperature is \(\Delta n = n_x - n_y = 0.65\). At \(-192\) °C, the refractive indices are ~10% lower than those at room temperature. It can be seen from Figure 3 that with the temperature change, the refractive index curves shift in parallel, practically without changing their shape.

The dispersion of the refractive indices in the range 0.2–1 THz for all temperatures is approximated in the form of Sellmeier equations:

\[
n_i^2 = A_i + \frac{B_i \lambda^2}{\lambda^2 - C_i}
\]  

where \(A_i\), \(B_i\), and \(C_i\) are the Sellmeier coefficients determined from the experimental data using the least-squares fit; \(i\) stands for \(x\), \(y\), \(z\); \(\lambda\) is the wavelength in \(\mu\)m. The behavior of the Sellmeier coefficients with respect to the temperature change is shown in Figure 4.

The data in Figure 4 show that the temperature dependences of Sellmeier coefficients are well approximated by linear functions:

\[
A_i(T) = A_{i0} + \delta A_i T \\
B_i(T) = B_{i0} + \delta B_i T \\
C_i(T) = C_{i0} + \delta C_i T
\]
The values of these coefficients obtained from experimental data are summarized in Table 1.

Table 1. The values of the Sellmeier coefficients.

| Axis | $A_0$ | $\delta_A \times 10^{-4}, \text{K}^{-1}$ | $B_0$ | $\delta_B \times 10^{-4}, \text{K}^{-1}$ | $C_0, \mu\text{m}^2$ | $\delta_C, \mu\text{m}^2\cdot\text{K}^{-1}$ |
|------|-------|---------------------------------|-------|---------------------------------|----------------|---------------------------------|
| x    | 8.89  | 7.32                            | 1.35  | 2.65                            | 12,848.15     | 1.28                            |
| y    | 9.14  | 9.36                            | 1.31  | 4.54                            | 12,857.17     | 1.68                            |
| z    | 11.08 | 22                               | 3.67  | 21.3                            | 10,566.31     | 0.83                            |

The absence of a strong deviation from the linear dependence may indicate that the change in the conduction mechanism in the crystal makes an insignificant contribution to the terahertz optical properties.

We also estimated the deviation of the optical axis direction in the studied spectral range. The value of the angle $V_Z$ is determined using the expression [24]:

$$\sin V_Z = \frac{n_z}{n_y} \sqrt{\frac{n_y^2 - n_z^2}{n_x^2 - n_z^2}}$$

(3)

where the refractive indices are taken from the approximation. Figure 5 shows the temperature dependence of $V_Z$ for the frequencies of 0.2 and 1 THz.

Figure 5. Temperature dependence of the $V_Z$ angle for 0.2 and 1 THz.

The angle $V_Z$ for 0.2 THz changes from 12.6° at the liquid nitrogen temperature to 16.1° at room temperature. In our previous measurements [4], the change in the angle $V_Z$ was 3.5 times smaller, from $V_Z = 17°$ at the liquid nitrogen temperature to $V_Z = 18°$ at room temperature.

4. Conclusions

This paper presented the results of the study of the optical properties of KTP crystals in the frequency range of 0.2–1 THz and the temperature range of (−192)–150 °C. The refractive indices of the optical indicatrix of the crystal were measured with linearly polarized terahertz radiation. The dispersion of the refractive indices was approximated in the form of Sellmeier equations. Experiments showed that the temperature dependence of the Sellmeier coefficients for all three crystal axes is close to linear. This indicated no extremum in the vicinity of the activation temperature of the ionic conductivity of the KTP crystal. The absorption coefficient $\alpha_z$ exhibited smooth dependence with respect to the crystal temperature. The absence of a broad weak absorption peak in the vicinity of 0.9 THz, which was observed in other studies, was most likely due to the better quality of the KTP crystal used in present study.
Based on the conducted studies, we conclude that the change in the mechanism of KTP electrical conductivity along the c-axis with its cooling influences the terahertz optical properties insignificantly. Therefore, this should not affect the nonlinear optical processes occurring within the terahertz range or based on interactions with phonons that are associated with vibrations of potassium sublattice.

Since the millimeter-wave range (<300 GHz) is free from strong absorption lines of atmospheric water, cooled high-quality KTP crystals can be of interest for developing a terahertz LiDAR. Indeed, KTP crystals have lower absorption and birefringence compared to the family of doped and undoped LiNbO$_3$ crystals [25] and can be used for efficient generation of THz radiation by collinear phase matching.

The change in $n_Z$ with cooling down to liquid nitrogen temperature is 0.12 in our case, which is comparable to its variation from crystal to crystal. We estimate this can lead to a shift in the phase-matching curves within 1° which can be considered insignificant for the case of free space optical alignment where it is possible to compensate for the difference by rotating the crystal. Otherwise, according to the phase-matching curves from [5], 1-degree detuning can lead to a significant shift in the generated difference frequency. Consequently, it should be taken into account for the correct design of nonlinear integrated terahertz photonic devices.

**Author Contributions:** Conceptualization, V.A.; spectra measurement and original draft preparation A.R. and V.A.; experimental data processing and analysis, A.R. and A.M.; writing—review and editing, N.N. and A.M.; supervision, N.N.; All authors have read and agreed to the published version of the manuscript.

**Funding:** The work is supported by the Russian Science Foundation, project No 17-12-01418.

**Informed Consent Statement:** Not applicable.

**Acknowledgments:** The authors thank P. L. Chapovsky and N. V. Surovtsev for useful suggestions and help in the manuscript preparation. The authors acknowledge the Shared Equipment Center CKP “Spectroscopy and Optics” of the Institute of Automation and Electrometry SB RAS for the provided terahertz spectrometer and the Shared Equipment Center CKP “VTAN” (ATRC) of the NSU Physics Department for the high-performance terahertz polarizers provided for measurements.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Bolt, R.J.; van der Mooreen, M. Single Shot Bulk Damage Threshold and Conversion Efficiency Measurements on Flux Grown KTiOPO$_4$ (KTP). Opt. Commun. 1993, 100, 399–410. [CrossRef]
2. Nikogosyan, D.N. *Nonlinear Optical Crystals: A Complete Survey*; Springer: New York, NY, USA, 2005; pp. 54–60. ISBN 0387220224.
3. Antsygin, V.D.; Kaplun, A.B.; Mamrashev, A.A.; Nikolaev, N.A.; Potaturkin, O.I. Terahertz Optical Properties of Potassium Titanyl Phosphate Crystals. Opt. Express 2014, 22, 25436. [CrossRef]
4. Mamrashev, A.; Nikolaev, N.; Antsygin, V.; Andreev, Y.; Lanski, G.; Meshalkin, A. Optical Properties of KTP Crystals and Their Potential for Terahertz Generation. Crystals 2018, 8, 310. [CrossRef]
5. Huang, J.-G.; Huang, Z.-M.; Nikolaev, N.A.; Mamrashev, A.A.; Antsygin, V.D.; Potaturkin, O.I.; Meshalkin, A.B.; Kaplun, A.B.; Lanski, G.V.; Andreev, Y.M.; et al. Phase Matching in RT KTP Crystal for Down-Conversion into the THz Range. Laser Phys. Lett. 2018, 15, 075401. [CrossRef]
6. Nikolaev, N.A.; Lansky, G.V.; Andreev, Y.M.; Ezhov, D.M.; Krekov, M.G.; Lisenko, A.A. β-BBO, LBO, AND KTP Nonlinear Crystals as Sources of Millimeter-Wave Radiation. Russ. Phys. J. 2020, 63, 1025–1029. [CrossRef]
7. Wu, M.-H.; Tsai, W.-C.; Chiu, Y.-C.; Huang, Y.-C. Generation of ~100 KW Narrow-Line Far-Infrared Radiation from a KTP off-Axis THz Parametric Oscillator. Optica 2019, 6, 723. [CrossRef]
8. Wu, M.-H.; Chiu, Y.-C.; Wang, T.-D.; Zhao, G.; Zukauskas, A.; Laurell, F.; Huang, Y.-C. Terahertz Parametric Generation and Amplification from Potassium Titanyl Phosphate in Comparison with Lithium Niobate and Lithium Tantalate. Opt. Express 2016, 24, 25964. [CrossRef]
9. Bigourd, D.; Cuisset, A.; Hindle, F.; Matson, S.; Fertein, E.; Bocquet, R.; Mouret, G. Detection and Quantification of Multiple Molecular Species in Mainstream Cigarette Smoke by Continuous-Wave Terahertz Spectroscopy. Optics Lett. 2006, 31, 2356. [CrossRef]
10. Hsieh, Y.D.; Nakamura, S.; Abdelsalam, D.G.; Minamikawa, T.; Mizutani, Y.; Yamamoto, H.; Iwata, T.; Hindle, F.; Yasui, T. Dynamic Terahertz Spectroscopy of Gas Molecules Mixed with Unwanted Aerosol under Atmospheric Pressure Using Fibre-Based Asynchronous-Optical-Sampling Terahertz Time-Domain Spectroscopy. Sci. Rep. 2016, 6, 28114. [CrossRef]

11. Mamrashev, A.A.; Maximov, L.V.; Nikolaev, N.A.; Chapovsky, P.L. Detection of Nuclear Spin Isomers of Water Molecules by Terahertz Time-Domain Spectroscopy. IEEE Trans. Terahertz Sci. Technol. 2018, 8, 13–18. [CrossRef]

12. Zhukov, S.S.; Balos, V.; Hoffman, G.; Alom, S.; Belyanchikov, M.; Nebioglu, M.; Roh, S.; Pronin, A.; Bacanu, G.R.; Abramov, P.; et al. Rotational Coherence of Encapsulated Ortho and Para Water in Fullerene-C60 Revealed by Time-Domain Terahertz Spectroscopy. Sci. Rep. 2020, 10, 18329. [CrossRef] [PubMed]

13. Nanni, E.A.; Huang, W.R.; Hong, K.H.; Ravi, K.; Fallahi, A.; Moriena, G.; Dwayne Miller, R.J.; Kärtner, F.X. Terahertz-Driven Linear Electron Acceleration. Nat. Commun. 2015, 6, 9486. [CrossRef]

14. Hafez, H.A.; Kovalev, S.; Tielrooij, K.; Bonn, M.; Gensch, M.; Turchinovich, D. Terahertz Nonlinear Optics of Graphene: From Saturable Absorption to High-Harmonics Generation. Adv. Opt. Mater. 2020, 8, 1900771. [CrossRef]

15. Cherkasova, O.P.; Serdyukov, D.S.; Ratushnyak, A.S.; Nemova, E.F.; Kozlov, E.N.; Shidlovskii, Y.V.; Zaytsev, K.I.; Tuchin, V.V. Effects of Terahertz Radiation on Living Cells: A Review. Opt. Spectrosc. 2020, 128, 855–866. [CrossRef]

16. Antsigin, V.D.; Gusev, V.A.; Semenenko, V.N.; Yurkin, A.M. Ferroelectric and Nonlinear Optical Properties of Ferroelectric-Superionic Ktp. Ferroelectrics 1993, 143, 223–227. [CrossRef]

17. Urenski, P.; Gorbatov, N.; Rosenman, G. Dielectric Relaxation in Flux Grown KTiOPo4 and Isomorphous Crystals. J. Appl. Phys. 2001, 89, 1850–1855. [CrossRef]

18. Kugel, G.E.; Brehat, F.; Wyncke, B.; Fontana, M.D.; Marnier, G.; Carabatos Nedelec, C.; Mangin, J. The Vibrational Spectrum of a Ktiop4 Single Crystal Studied by Raman and Infrared Reflectivity Spectroscopy. J. Phys. C Solid State Phys. 1988, 21, 5565–5583. [CrossRef]

19. Wu, Q.; Zhang, X.C. Free-Space Electro-Optic Sampling of Terahertz Beams. Appl. Phys. Lett. 1995, 67, 3523. [CrossRef]

20. Mamrashev, A.A.; Potaturkin, O.I. Characteristics of the System of Polarization-Optical Detection of a Pulsed Terahertz Spectrometer. Optoelectron. Instrum. Data Process. 2011, 47, 332–337. [CrossRef]

21. Duvillaret, L.; Garet, F.; Coutaz, J.L. A Reliable Method for Extraction of Material Parameters in Terahertz Time-Domain Spectroscopy. IEEE J. Sel. Topics Quantum Electron. 1996, 2, 739–745. [CrossRef]

22. Surovtsev, N.V.; Malinovskii, V.K.; Pugachev, A.M.; Shebanin, A.P. The Nature of Low-Frequency Raman Scattering in Congruent Melting Crystals of Lithium Niobate. Phys. Solid State 2003, 45, 534–541. [CrossRef]

23. Mounaix, P.; Sarger, L.; Caumes, J.P.; Freysz, E. Characterization of Non-Linear Potassium Crystals in the Terahertz Frequency Domain. Opt. Commun. 2004, 242, 631–639. [CrossRef]

24. Dmitriev, V.G.; Gurzadyan, G.G.; Nikogosyan, D.N. Handbook of Nonlinear Optical Crystals. In Optical Sciences; Springer: Berlin/Heidelberg, Germany, 1991; Volume 64, p. 16; ISBN 978-3-662-13832-8.

25. Pálfalvi, L.; Hebling, J.; Kuhl, J.; Péter, A.; Polgár, K. Temperature and Composition Dependence of the Absorption and Refraction of Mg-Doped Congruent and Stoichiometric LiNbO3 in the THz Range. In Proceedings of the Optics InfoBase Conference Papers, Optical Society of America (OSA), Vienna, Austria, 6 February 2005; p. WB4.