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Index of Refraction and Absorption Coefficient Spectra of Paratellurite in the Terahertz Region

Márta Unferdorben[1] · Andrea Buzády[1] · János Hebling[1,2,3] · Krisztián Kiss[1] · Ivett Hajdara[4] · László Kovács[4] · Ágnes Péter[4] · László Pálfalvi[1]

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Abstract Index of refraction and absorption coefficient spectra of pure paratellurite (α-TeO_2) crystal as a potential material for terahertz (THz) applications were determined in the 0.25–2 THz frequency range at room temperature by THz time domain spectroscopy (THz-TDS). The investigation was performed with beam polarization both parallel (extraordinary polarization) and perpendicular (ordinary polarization) to the optical axis [001] of the crystal. Similarly to the visible spectral range, positive birefringence was observed in the THz range as well. It was shown that the values of the refractive index for extraordinary polarization are higher and show significantly larger dispersion than for the ordinary one. The absorption coefficient values are also larger for extraordinary polarization. The measured values were fitted by theoretical curves derived from the complex dielectric function containing independent terms of Lorentz oscillators due to phonon-polariton resonances. The results are compared with earlier publications, and the observed significant discrepancies are discussed.

Keywords Paratellurite · Terahertz frequency range · Refractive index · Absorption coefficient · Time domain terahertz spectroscopy

✉ Márta Unferdorben
umarta@fizika.ttk.pte.hu

1 Institute of Physics, University of Pécs, H-7624Ifjúság útja 6., Pécs, Hungary

2 MTA-PTE High-Field Terahertz Research Group, H-7624Ifjúság útja 20., Pécs, Hungary

3 Szentágothai Research Centre, University of Pécs, H-7624Ifjúság útja 20., Pécs, Hungary

4 Wigner Research Centre for Physics, Hungarian Academy of Sciences, H-1121XII. Konkoly Thege Miklós út 29-33., Budapest, Hungary

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1 Introduction

α-TeO_2 has attracted considerable attention from the point of view of both fundamental sciences and applications because of its remarkable acousto-optical and electro-optical properties. α-TeO_2 crystallizes in the P4 ($4_1 2_1 2$) space group, with tetragonal symmetry in a distorted rutile type cell doubled along the c axis. This structure is composed of considerably deformed TeO_6 octahedra, including alternating weak and strong bonds in the Te-O chains [1, 2]. Following from the high degree of 422 class symmetry, in the elastic tensor, similarly to the case of polarized ferroelectrics only the c_{66} element (which is independent of c_{11} and c_{12}) describes the absence of cylindrical symmetry of the elastic tensor about the c axis. The piezoelectric tensor shows complete rotational symmetry by consisting of only two non-vanishing shear elements (e_{14} = -e_{25}), excluding the piezoelectric excitation of longitudinal modes. The second-order nonlinear optical susceptibility tensor also has a simple form as $\chi_{yzx} = \chi_{yxz} = -\chi_{xyz} = -\chi_{xzy}$.

α-TeO_2 is a congruently melting material and can be grown in optical quality by the Czochralski technique. Single crystals are colorless and transparent in the 0.33–6.5 μm region [3]. It is a positive uniaxial material showing optical activity for light propagating along the optical axis [4] and has a large second-order nonlinear optical coefficient in the transparent frequency region (values of d_{14} = 0.59 pm/V [5] or d_{14} = 0.69 pm/V [6] at 1064 nm). Nonlinear optical properties of the material are also discussed in Ref. [7]. The unique polarizability properties of α-TeO_2 are manifested in the extremely high response of its electronic subsystem to deformation and external electric field. The only non-zero electro-optic coefficient r_{41} measured at constant stress was found to be -0.76 pm/V. The secondary electro-optic effect, due to the converse piezoelectric and photoelastic effects, is nearly twice as large as the observed electro-optic response [8].

In the past 20 years materials research has provided new and high-power sources in the terahertz (THz) frequency region and demonstrated the potential of THz-systems both for advanced physics research and commercial applications implying diverse sectors as the semiconductor, medical, space, and defense industries. Pulsed THz sources are based on the excitation of their material with ultrashort laser pulses. The two most common approaches for THz beam generation are based on the application of photoconduction and optical rectification using various types of semiconductors (e.g., Te, GaAs, InP, InSe) and non-linear optical materials (e.g., $LiNbO_3$/$LiTaO_3$), respectively [9].

There is still significant research interest in the search for suitable novel materials. Sotome and co-workers have only recently reported the generation of THz radiation in α-TeO_2 single crystals irradiated with 800 nm wavelength femtosecond laser pulses [10].

Design and development of α-TeO_2 based THz sources requires the precise knowledge of its absorption coefficient and index of refraction in the THz range. These parameters are also interesting for linear terahertz spectroscopy applications, for example due to its birefringence the material is a potential candidate for using in phase retardation plates. Although the absorption coefficient and index of refraction spectra have already been determined by THz-TDS, as shown in Fig. 2 of Ref. [10], the precise determination of data from their plot is problematic and the correspondence of the measured data with the theoretical curves is unsatisfactory. In this paper, we report the results of THz-TDS measurements of α-TeO_2 grown in the Wigner Research Centre for Physics, Budapest. A theoretical fitting of the absorption coefficient and index of refraction spectra by a function containing several Lorentz

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oscillator terms due to phonon-polariton resonances is also given. The relation of the results with those of Ref. [10] is also discussed.

2 Measurement Methods

High quality, defect free paratellurite single crystals with 28 mm diameter and 58 mm length along the [110] direction were grown by the balance-controlled Czochralski method using platinum crucible and resistance heating [11]. The raw material was TeO_2 powder prepared from Te metal with impurity content lower than 5 ppm. The crystals were oriented by X-ray diffraction and cut along the [110] and [001] directions to a typical size of about $7 \times 8 \times 0.5$ mm^3. High quality optical surfaces were polished. The precise thickness of the pure plane-parallel plate α-TeO_2 crystals was measured to be 480 μm with a micrometer having a resolution of 5 μm.

The index of refraction $n(\nu)$ and absorption coefficient $\alpha(\nu)$ spectra of paratellurite were determined in the 0.25–2 THz frequency range at room temperature by THz time domain spectroscopy (THz-TDS). For the examination, a TERA K8 terahertz spectrometer (Menlo Systems) was used. To avoid the absorption of water vapor, nitrogen gas was circulated in the spectrometer keeping the humidity around 7 % [12]. Because of the well-known birefringence of α-TeO_2 in the visible frequency range [4], measurements were performed with beam polarization both parallel (extraordinary polarization) and perpendicular (ordinary polarization) to the optical axis [001] of the crystal. Since the polarization of the THz antenna source was not perfectly linear, a week beating-like modulation [13, 14] was observed in the spectra. The period of the modulation was in accordance with the magnitude of the birefringence. In order to avoid this effect, a wire grid polarizer was placed between the source and the sample.

In the course of the measurements, the time dependence of the THz electric field was monitored with and without the sample; the respective fields are shown as $e_{samp}(t)$ (solid) and $e_{ref}(t)$ (dashed) in Fig. 1. As seen, the temporal shape of $e_{samp}(t)$ consists of a main peak followed by weaker ones due to Fabry-Perot (FP) reflections.

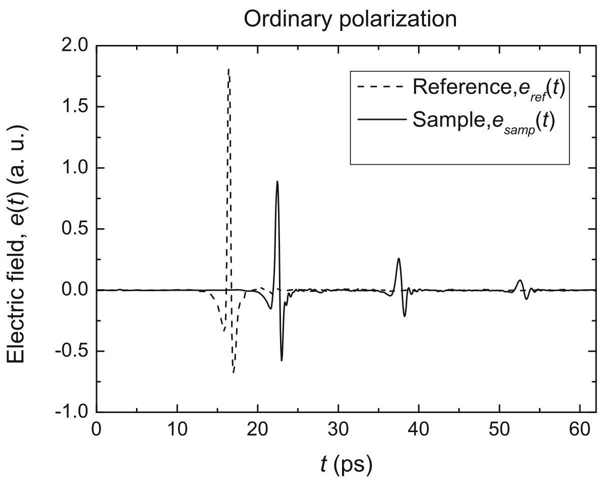

Fig. 1 The measured THz pulses with (*solid*) and without (*dashed*) the α-TeO_2 sample

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Determination of the refractive index and absorption coefficient spectra from the temporal curves was performed by the TeraMat software (Menlo Systems) belonging to the spectrometer. Since the software is unable to take into account the FP effect, the time window was shut before the arrival of the first reflected pulse at 34 ps (see Fig. 1). The software automatically completed the curve with zero values (zero padding) [15] to restore the original time window width of 62.5 ps resulting in a spectral resolution of 0.016 THz. After performing Fast Fourier Transform and taking into account the sample thickness, the software generates $n(\nu)$ and $\alpha(\nu)$ as outputs. Three measurements were performed for each polarization.

3 Results and Discussion

The index of refraction and absorption coefficient spectra were determined from the temporal curves (shown in Fig. 1 for ordinary polarization as an example) with the TeraMat software. The average of three spectra is plotted in Fig. 2 for both ordinary and extraordinary polarizations by dotted lines. The error of the measurements is shown by error bars.

As it is obvious from Fig. 2a–d, a monotonous increase with frequency can be observed for both the index of refraction and the absorption coefficient data for both polarizations. In the frequency range examined, the extraordinary index of refraction values are larger than those

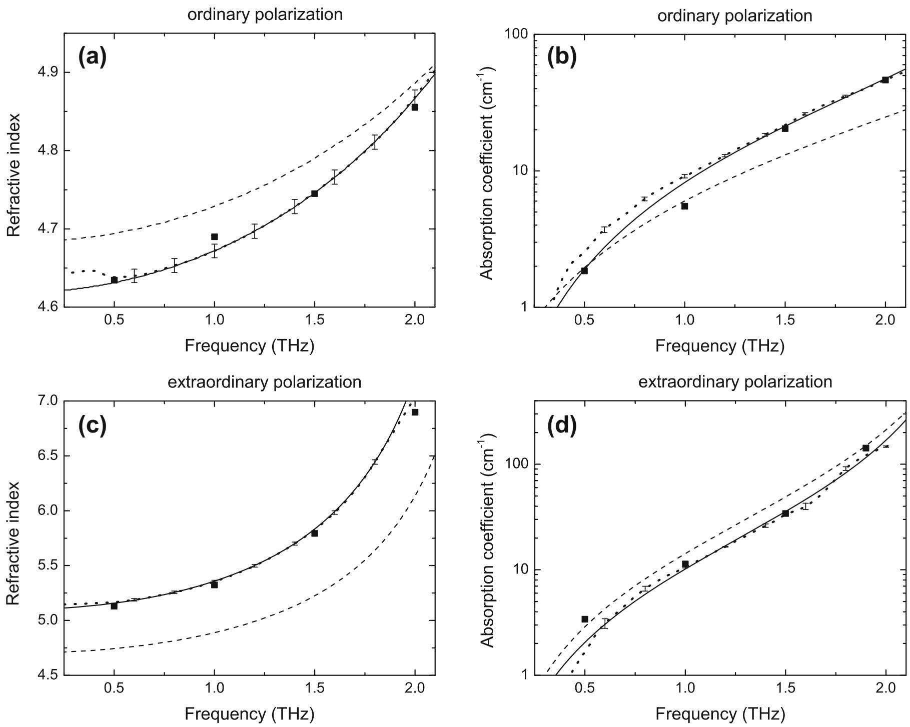

Fig. 2 Index of refraction and absorption coefficient values of α-TeO_2 belonging to ordinary (**a**, **b**) and to extraordinary (**c**, **d**) polarization. In all four cases, the *dotted curves* show our measured spectra, *squares* show the data measured by Sotome et al. The *solid curves* represent the fitting of our measured spectra by the Lorentz model, the *dashed curves* are calculated by Sotome et al. from the Lorentz model fitting of their reflectance curves. Please notice the logarithmic vertical scale in parts (**b**) and (**d**)

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for ordinary polarization maintaining the nature of positive birefringence as observed earlier in the visible range [4]. Comparing the dotted curves of Fig. 2a, c, it is also seen that the dispersion is about seven times larger for the extraordinary polarization than for the ordinary one. As seen in Fig. 2b, d, the absorption coefficient values are also larger for extraordinary polarization.

It is worth mentioning that the polarization dependence of both the index of refraction and the absorption coefficient of α-TeO_2 have opposite character compared to that of $LiNbO_3$. $LiNbO_3$ has negative birefringence and smaller extraordinary absorption compared to ordinary both in the optical and in the THz ranges [16, 17].

In the THz range, the complex dielectric function of α-TeO_2 is practically determined by the phonon-polariton resonances and can be expressed as a sum of N Lorentz oscillators [10]. Accordingly, the complex dielectric function can be given as

$$\in(\nu) = \epsilon_\infty + \sum_{i=1}^{N} \frac{f_i \nu_i^2}{\nu_i^2 - \nu^2 - j\gamma_i\nu}, \tag{1}$$

where ϵ_∞, ν_i, γ_i and f_i represent the high-frequency dielectric constant, the resonance frequency, the damping coefficient, and the oscillator strength for each of the N oscillators, respectively. The $n(\nu)$ index of refraction is the real part of the $n^\sim(\nu) = \sqrt{\epsilon^\sim(\nu)} = n(\nu) + j\kappa(\nu)$ complex index of refraction, and the absorption coefficient can be determined as $\alpha(\nu) = \frac{4\pi\nu}{c_0}\kappa(\nu)$, where c_0 is the speed of light in vacuum.

Measured reflectance curves of α-TeO_2 with their fittings using the Lorentz oscillator model (Eq. 1) have been reported in reference [10]. Similarly as in Ref. [18], the upper bound of the range examined by them is also near 24 THz and the number of oscillator terms considered in the dielectric function is also $N=8$ for ordinary and $N=4$ for extraordinary polarization. The values of the fitting parameters ((ν_i, γ_i and f_i) are collected in Table 1 where normal font numbers are the values of Table 3 of Ref. [10]. The resonance frequency values determined by Sotome et al. [10] are very similar to those of earlier Raman and far-

Table 1 Fitting parameters of the Lorentz oscillator model

Mode i	Polarization	ν_i (THz)	γ_i (THz)	f_i
1	Ordinary	3.660	0.111; *0.500*	0.654; *2.569*
2		5.314	0.155	6.958; *4.890*
3		6.400	0.361	2.404; *2.160*
4		9.052	0.310	4.181
5		9.797	0.495	0.574
6		11.730	1.064	0.071
7		18.830	0.561	1.655; *1.450*
8		22.930	0.498	0.184
1	Extraordinary	2.534; *2.460*	0.15; *0.075*	9.436; *13.338*
2		7.804	0.375	0.659
3		9.652	0.306	3.760
4		18.140	0.685	2.873

Normal font: values obtained from fitting the reflectance curves of [9], italic type: modified values for eight cases required by the fitting of our measured refractive index and absorption values

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infrared studies [18–20]. The value of the high-frequency dielectric constant is $\epsilon_\infty = 5.25$ and 5.38 for ordinary and extraordinary polarization, respectively. The refractive index and absorption coefficient spectra calculated from Eq. (1) using the parameters of Table 1 (normal font numbers) are shown in Fig. 2a–d with dashed line.

In Ref. [10], refractive index and absorption coefficient curves obtained from THz-TDS measurements are plotted in a lower frequency region. Some of these data are also added to Fig. 2a–d (squares) at a few frequencies, although the reconstruction of the values from the graph of Ref. [10] was of limited. These data are in good agreement with our measured values (dotted). But as seen in Fig. 2c, d of Ref. [10] and also seen in Fig. 2a–d of the present paper, there is significant mismatch between the measured values (squares in Fig. 2 of this paper) and the curves (dashed lines in Fig. 2 of this paper) derived from the Lorentz model fitted to the reflectance curves measured by Sotome et al.

THz-TDS is advantageous at low frequencies under 3 THz, while FIR FT spectroscopy works better at frequencies above 5 THz [21]. In order to fit precisely the measured THz-TDS data in the 0.25–2 THz frequency range and also to be consistent with the high frequency FIR FT reflectance data (determined by Sotome et al.), the modification of some Lorentz-model parameters (Table 1) is needed. This means the modification of eight parameters (Table 1) of the parameter set determined by Sotome. In Fig. 2, the solid lines represent the fitting curves corresponding to the Lorentz-function with modified parameters in all cases. The modified values are shown by bold typed numbers in Table 1. In Table 1, only one resonance frequency value (ν_1 for extraordinary polarization) was changed, its modified value equals to the corresponding frequency of Ref. [18]. The other modified values belonging to the extraordinary polarization are also identical or very close to the corresponding values of Ref. [18].

The successful fitting of our and Sotome's THz-TDS data demonstrates that in the low THz region, the parameters of these fitting are much more reliable than the ones derived from the far-infrared reflectance fittings. From Eq. (1) together with the (modified) parameters given in Table 1, one can determine easily the ordinary and extraordinary index of refraction and absorption coefficient spectra of α-TeO_2 in the 0.25–2 THz frequency range with high accuracy.

The Lorentz model with the modified parameters is also consistent with the FIR FT results of Sotome et al. at higher frequencies. In Fig. 3a, b, calculated reflectance curves are shown for ordinary and extraordinary polarizations, respectively. In both cases, the dashed curves are the result of fitting the FIR FT reflectance curves [10] and are calculated from the unmodified

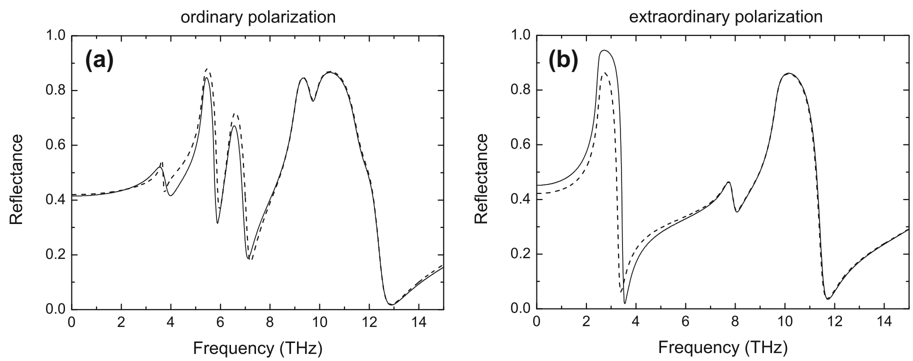

Fig. 3 Reflectance curves deduced from the Lorentz model for ordinary (**a**) and extraordinary polarization (**b**). The *dashed lines* correspond to the unmodified, the *solid lines* to the modified parameters of Table 1

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parameters of Table 1. The solid curves in both cases are calculated from the modified parameters of Table 1. At high frequencies, where the FIR FT spectroscopy method is more adequate, good agreement can be found between the reflectance curves.

4 Conclusion

THz-TDS measurements were performed on α-TeO_2 for beam polarization parallel and perpendicular to the crystal optical axis at room temperature. The index of refraction and absorption coefficient values were determined as functions of frequency in the 0.25–2 THz range. The index of refraction and absorption coefficient values were calculated by the TeraMat software belonging to the spectrometer. Theoretical fitting with the Lorentz model was performed resulting in analytical functions describing the index of refraction and absorption coefficient in the 0.25–2 THz frequency range. The presented results are a refinement of index of refraction and absorption coefficient data published earlier [10].

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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