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Basic spectroscopic properties of bismuth tellurium oxide, Bi_2TeO_5

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Optical absorption measurements in the visible and infrared and reflectivity measurements in the visible and ultraviolet are reported for single crystals of bismuth tellurium oxide (Bi_2TeO_5). Strong dependence of these measurements on the light polarization is found for this recently grown non-linear material. Deviation from the Urbach rule (see Appendix) is believed to result from non-stoichiometry; approximate values of the Urbach parameters are given for the [0 1 0] polarization.

1. Introduction

Bismuth tellurium oxide (Bi_2TeO_5) is a new non-linear optical material. After several early attempts to separate defined compositions in the rather complex phase diagram of the Bi_2O_3–TeO_2 system [1–5], Simon *et al.* [6] have pointed out the prospective advantages of the Bi_2TeO_5 composition. This specific compound crystallizes in an orthorhombic structure with the C_{2v}^{15} space group. The unit cell can be described as a $2 \times 3 \times 1$ multiplication of a fluorite-type structure where the cation positions are filled alternately with Bi and Te ions [7]. Simon *et al.* also showed that the Bi_2TeO_5 crystals exhibit interesting non-linear properties, based upon preliminary results from microcrystalline samples [6].

Large single crystals of Bi_2TeO_5, suitable for optical investigations, have recently been grown in the Research Laboratory for Crystal Physics, Budapest; the growth procedure for these crystals has been reported and also measurements of the optical transparency range (0.4–7 μm) and the density (7.91 g cm^{-3}) [8]. Earlier, unpolarized room temperature (RT) absorption spectra were published in the visible and infrared region for Bi_2TeO_5 [9]. These data, however, reflect strong extrinsic absorption and the homogeneity and impurity level of the crystals were not discussed. Detailed investigations of the electrical conductivity and dielectric properties of the crystal have been presented by Avramenko *et al.* [10]. Experiments have shown that Bi_2TeO_5 single crystals also have interesting photorefractive properties [11]; further investigations are required, however, to determine the optimum photorefractive conditions and clarify the mechanism of the process. The purpose of the present work is to report basic optical data for Bi_2TeO_5 crystals which can be useful for non-linear optical research and possible applications employing this material.

2. Experimental procedure

The raw materials Bi_2O_3 and TeO_2 were prepared from 99.999% pure metal rods by chemical digestion at the Research Laboratory for Crystal Physics. The Bi_2TeO_5 compound was prepared from the basic oxides by a solid state reaction and single crystals of Bi_2TeO_5 were grown in air by the Czochralski method [8]. The typical boule diameter was between 15 and 25 mm, which is suitable for most optical measurements. Chemical analysis by atomic absorption spectroscopy has detected low impurity levels (e.g., 20 p.p.m. for Fe and 2 p.p.m. for Cr) in these crystals. Use of commercial sources, which provided only moderate quality starting materials, resulted in brownish-coloured crystals that exhibited optical absorption due either to impurities or to a deviation from the desired composition. The detected impurity level for chromium was 30 p.p.m. in the less pure brownish crystals.

Bismuth tellurite has a (1 0 0) cleavage plane along which mirror flat surfaces could be obtained. The practical lower limit of thickness for the absorption measurements was about 0.08 mm. With thicker samples (> 0.5 mm) large surface areas (4–6 cm^2) were available meeting the demands of the reflectivity measurements. In all investigations freshly cleaved

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samples were used. Reflectivity spectra were measured at the University of Connecticut at RT on a Cary 14 R spectrophotometer. Its reflection chamber permitted a determination of the absolute reflectivity of the crystals without a reference standard. The visible range absorption spectra were measured at this laboratory on a Perkin-Elmer Lambda 4 spectrophotometer equipped with an APD Displex closed-cycle helium refrigerator operable over a 10–300 K temperature range. The infrared spectra were measured at the University of Parma on a Jasco DS 702-G spectrophotometer. A 21-SC Cryodine Cryocooler (CTI Cryogenics) was used to permit measurements in this same temperature range.

Various standard methods were used to analyse the spectroscopic data. In the reflectivity spectra the data were corrected for the backside interface and multiple reflection. For the RT absorption measurements in the visible range, multiple reflection from the front and back interfaces was corrected by using the measured reflectivity data. The low temperature absorption measurements were performed using two different sample thicknesses and the reflection loss was calculated by fitting the two data sets. In the treatment of infrared measurements a smoothing of the curves was performed because interference patterns were obtained with the thin crystals. The interface reflection was corrected by using samples of different thickness and the same fitting methods were used as for the visible range spectra. The equations used for the spectrum corrections are summarized in the Appendix.

3. Results and Discussion

Reflectivity spectra of Bi_2TeO_5 at RT are depicted in Fig. 1 for two polarization directions parallel to the cleaved (1 0 0) surface. A substantial anisotropy in the reflectivity is evident from a comparison of the $\vec{E}\parallel[001]$ and $\vec{E}\parallel[010]$ polarization spectra. The high reflectivity and its strong variation with wavelength are in accordance with expectations for a high density oxide crystal consisting of heavy elements. The reflectivity spectra of the brownish crystals grown from commercial starting material are not appreciably different from that of the higher purity crystals.

In the infrared spectra we have not found absorption bands characteristic for an OH^- stretching vibration. The OH^- frequency in oxides is typically situated within the 3800–3000 cm^{-1} energy range. The incorporation of OH^- ions in oxide crystals is connected with their role in the charge compensation of impurities or defects in the host lattice. The absence of the OH^- absorption in the Bi_2TeO_5 crystal may be due to the low impurity level or to the special structure of the crystal. It was shown that the deviation from the Bi_2TeO_5 composition toward the Te rich direction resulted in a monotonous change in the crystal composition which did not require point defect type charge compensation [7, 12]. Kucha *et al.* have found relatively strong absorption in the unpolarized RT spectra at 2850 and 2140 cm^{-1} [9]. These band positions are both at lower energy than that which is typical for OH^- absorption in oxides. Thus we think that they belong to compositional defects or impurities rather than to OH^-.

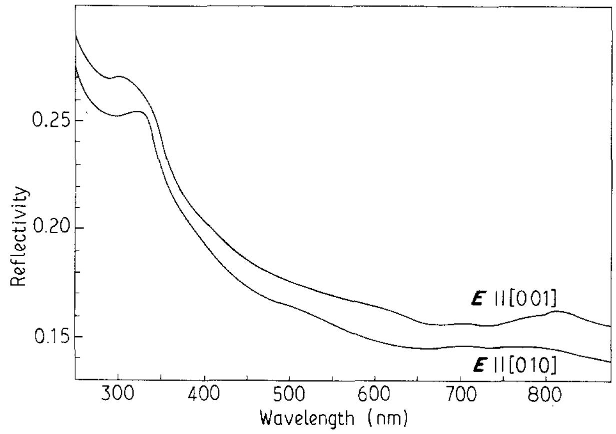

Figure 1 Reflectivity spectra of Bi_2TeO_5 single crystals at room temperature (RT). The polarization directions correspond to basic crystallographic directions perpendicular to the cleaved (1 0 0) surfaces of the samples.

An extended region of the intrinsic absorption could be followed by i.r. absorption spectroscopy on very thin crystal samples. The RT and 10 K infrared absorption spectra of Bi_2TeO_5 in this region are shown in Fig. 2. Besides the broad, low intensity bands in the 2400–1600 cm^{-1} range, intense bands were observed in the 1500–900 cm^{-1} range and the leading edge of another one which was situated below 850 cm^{-1}. The fine structure of these bands was observable even at RT. In the 10 K measurements sharp lines and additional shoulders appeared in the spectral range below 1600 cm^{-1}. The positions of the lines and shoulders of the infrared absorption at 10 K are collected in Table I. The absorption coefficients in Table I are measured values at the given wave numbers, without taking into account overlapping of the bands. The polarized spectra in this region are shown in Fig. 3. These spectra clearly indicate significant anisotropy and the number of resolvable bands is higher than that observed in the unpolarized infrared spectra. The data for the polarized infrared spectra are also presented in Table I. Kucha *et al.* published unpolarized RT spectra for these same energy ranges [9], however, they have not corrected for the interference pattern.

Visible range absorption spectra of the Bi_2TeO_5 single crystals are shown in Fig. 4. These spectra have been corrected for multiple reflections. The position of the absorption edge is dependent upon the polarization direction at both RT and low temperature. In all cases the absorption edge occurs at shorter wavelength in the [0 1 0] polarization direction than in the [0 0 1] direction. When the crystals were grown from high purity raw materials, no significant absorption was observed in the transparent spectral range. The pale yellow colouration of these crystals is likely due to the tail of the absorption edge. The brownish-coloured crystals, in which a higher impurity content was detected, have enhanced absorption near the absorption edge and in the 650–850 nm region. Net absorption in the visible range for the crystal studied

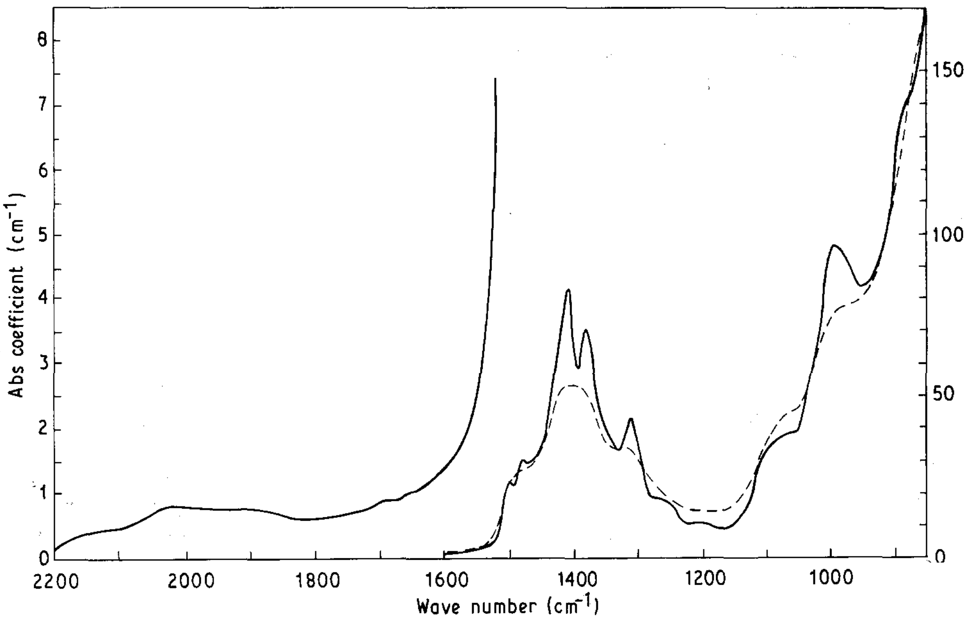

Figure 2 Infrared absorption spectra of Bi_2TeO_5 single crystals measured at RT (dashed line) and 10 K (solid line). The thickness of the samples in the different spectral regions varied from 0.095 to 16 mm.

TABLE I Position and absorption coefficients of the bands in regular and polarized infrared absorption spectra of Bi_2TeO_5 single crystals

300 K pos. (cm^{-1})	Abs. coefficient (cm^{-1})	10 K pos. (cm^{-1})	Abs. coefficient (cm^{-1})	Polarized, 10 K [0 1 0] pos. (cm^{-1})	Abs. coefficient (cm^{-1})	[0 0 1] pos. (cm^{-1})	Abs. coefficient (cm^{-1})
		2125	0.5				
		2020	0.8				
		1940	0.7				
		1690	0.9				
		1650	1.0				
		1495	23			1495	21
1470	28	1480	30	1480	38	1480	22
						1420	71
1410	53	1405	83	1405	74		
		1380	70	1382	72	1390	53
				1335	49		
1320	34	1310	43	1315	61	1308	28
		1270	18			1265	21
		1200	10	1200	12	1200	11
				1120	25		
				1092	34	1092	36
1060	45	1070	38			1075	43
970	78	995	96	995	88	995	112
						965	100
				910	170		
		875	142	875	211	875	135

by Kucha *et al.* [9] is still higher, reflecting high impurity level or mixed composition of the crystals studied.

The temperature dependence of the absorption edge in the [0 1 0] polarization direction is shown in Fig. 5. To check the validity of applying the Urbach rule the absorption coefficient (α) is plotted on a logarithmic scale as a function of photon energy (E) at temperatures of 10, 77 and 300 K (see details for application of the Urbach rule in the Appendix). The deviation of the plot of log α versus E from linearity below the 50 cm^{-1} absorption level suggests that the absorption is not entirely intrinsic. High purity oxide materials regularly obey the Urbach rule down to 10 cm^{-1} and often down to 1 cm ^{1}. Extensive deviation, such as that observed for Bi_2TeO_5, is typical for high impurity content. However, based on impurity analyses of our samples this is an unlikely cause of the deviation. It was shown in an earlier paper for $LiNbO_3$ crystals that increased non-stoichiometry influences the absorption edge similarly to increased impurity concentration [13]. In a like manner, the observed deviation from the Urbach rule for our Bi_2TeO_5 crystals may be connected with their non-stoichiometric character. The large variety of possible Bi_2O_3–TeO_2 phases and the incommensurable intergrowth of

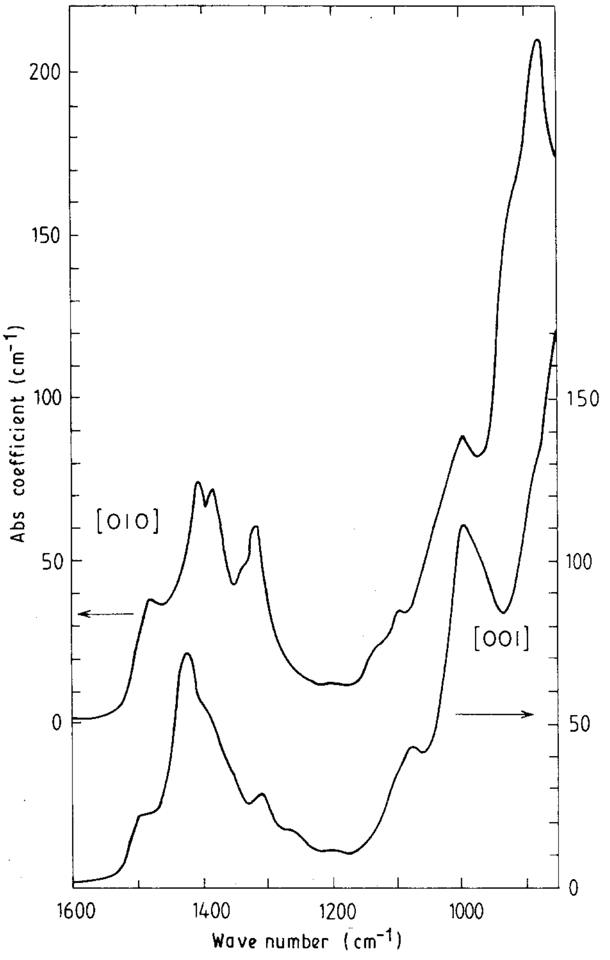

Figure 3 Polarized infrared spectra of Bi_2TeO_5 single crystals measured at 10 K. The $\vec{E}$ polarization directions are indicated.

Bi_2TeO_5 and $Bi_2Te_2O_7$ structures support this idea [7] and [12]. We do not have direct evidence for any alteration from the precise Bi_2TeO_5 composition in our crystals since the classical wet chemical analysis used was not adequate for determining small changes in the crystal composition [8].

The relatively short linear range of the log α versus E plot has permitted a calculation of only approximate values of the Urbach parameters which are: $\alpha_0 = 10^9$ cm^{-1}, $E_0 = 3.8$ eV in the [0 1 0] polarization direction (for notations, see Appendix). In the [0 0 1] polarization the deviation of log α versus E from a straight line was even more pronounced and no reliable values for E_0 and α_0 were determined.

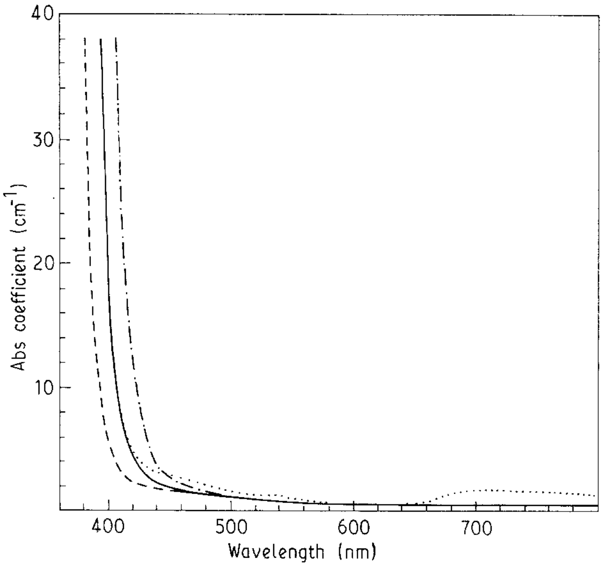

Figure 4 Optical absorption spectra of Bi_2TeO_5 single crystals in the visible region. Anisotropy of the band edge with polarization: (–·–) is [0 0 1] and (—) is [0 1 0] polarized spectra at RT. The shift of the band edge with temperature is illustrated with the RT (—) and 10 K (– – –) spectra measured at [0 1 0] polarization. For comparison the plot represented by dots is the [0 1 0] spectrum at RT of the nominally pure brownish crystal prepared from commercial materials.

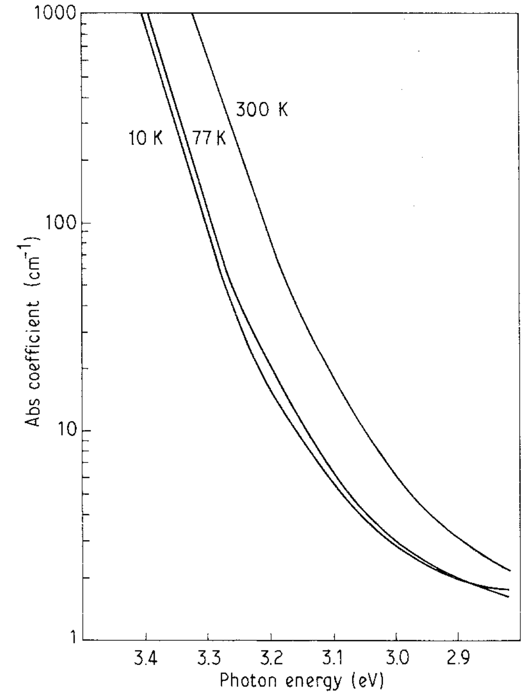

Figure 5 Temperature dependence of the absorption edge of Bi_2TeO_5 single crystals measured in the [0 1 0] polarization direction.

4. Summary

Reflectivity spectra of Bi_2TeO_5 single crystals were measured in the 250–900 nm spectral range for [0 1 0] and [0 0 1] polarization directions at 300 K. Optical absorption measurements covered the absorption edge and transparent region over a temperature range of 10–300 K. The observed strong deviation from the Urbach rule is believed to be due to the non-stoichiometric character of the crystals. In the infrared region the fine structure of the intrinsic i.r. absorption was studied over the same temperature range. In all of the polarized measurements, strong anisotropy was detected between the [0 1 0] and [0 0 1] crystallographic directions. The observed optical anisotropy in this low symmetry crystal supports the idea that the material should exhibit characteristic non-linear properties.

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Appendix

Formulas used for analysis of spectra:

1. Correction for the multiple reflection from the front and back surfaces of the crystal at a given wavelength is given by

$$I = I_0 \frac{(1 - R)^2 e^{-\alpha x}}{1 - R^2 e^{-2\alpha x}} \tag{1}$$

where I_0 and I are the incident and transmitted intensities, respectively. In this equation α is the absorption coefficient, x is the thickness of the crystal and R is the single reflectivity. One should note that α and R are temperature dependent parameters.

2. The Urbach equation in Toyozawa's interpretation [14, 15] is

$$\alpha = \alpha_0 e^{-S(E_0 - E)/kT} \tag{2}$$

where α is the actual absorption coefficient at temperature T and photon energy E, α_0 and E_0 are the coordinates of the cross-over point of the extrapolated lines of the absorption edge at various temperatures, S is a temperature dependent parameter characterizing the exciton–phonon interaction and k is the Boltzmann constant.

3. The specular reflectivity R_1 is calculated from the equation for the multiple reflectivity R_m from a thin sample. R_m is given by

$$R_m = R_1 + (1 - 2R_1 + R_1^2)R_2 \tag{3}$$

where R_1 and R_2 are the reflectivities of the first and second surfaces.

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