Comparative Study of Bismuth Tellurites by Infrared Absorption Spectroscopy

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Infrared spectra of α-$Bi_2Te_4O_{11}$, β-$Bi_2Te_4O_{11}$, $Bi_2Te_2O_7$, and Bi_2TeO_5, have been compared and analyzed. The bands in the region of 620–400 cm^{-1} correspond to the stretching modes of the bismuth–oxygen framework, while those in the region of 800–620 cm^{-1} belong to the stretching vibrations of the Te–O bonds. TeO_3 polyhedra of trigonal–pyramidal configuration with equal bond lengths (within 0.02 nm) have been found in bismuth tellurites. The largest deformation of TeO_3 has been observed in Bi_2TeO_5 as compared to the other bismuth tellurites investigated in this study. Connected TeO_3 polyhedra form Te_2O_5 groups in the structure of α-$Bi_2Te_4O_{11}$. The relation between the frequency of the asymmetric stretching mode and the length of Bi–O bond is linear for Bi_2TeO_5 and nonlinear for α-$Bi_2Te_4O_{11}$ and α-Bi_2O_3. © 2000 Academic Press

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INTRODUCTION

Bismuth-oxide-based compounds have a number of important applications. The δ-Bi_2O_3-type compounds have anion-deficient fluorite structures and are applied as oxygen ion conductors (1, 2). The bismuth tellurium oxides such as β-$Bi_2Te_4O_{11}$, $Bi_2Te_2O_7$, and Bi_2TeO_5 structurally belong to the δ-Bi_2O_3-type compounds (3, 4). Among them the most important is Bi_2TeO_5, which shows peculiar photorefractive properties (5). $Bi_2Te_4O_{11}$ has two modifications: β-$Bi_2Te_4O_{11}$ belongs to the δ-Bi_2O_3 type compounds while α-$Bi_2Te_4O_{11}$ is similar to α-Bi_2O_3 (3). The monoclinic α-Bi_2O_3 is stable up to 729°C and above this temperature it transforms to δ-Bi_2O_3. On cooling δ-Bi_2O_3, two metastable modifications may occur, i.e., the tetragonal β-Bi_2O_3 and the bcc γ-Bi_2O_3 phase. The γ-Bi_2O_3-type compounds are called sillenites and can be written by the formula of $Bi_{12}MO_{20}$ (M = Ge, Si, Ti). Due to the piezoelectric, elec-

trooptical, and elastooptical properties they have many technological applications (6).

The aim of this work is to characterize bismuth tellurite compounds by infrared spectroscopy and compare the results with other structural investigations. As a starting point the IR-spectra of α-Bi_2O_3 and α-TeO_2 are revisited.

The monoclinic alpha Bi_2O_3 contains two sorts of bismuth atoms. One of them has five oxygen neighbors at the corners of a distorted octahedron with the inert pair of electrons occupying the sixth corner (the lengths of Bi–O bonds are placed between 0.21 and 0.26 nm). Two more oxygen atoms are weakly bonded (0.32 nm, 0.34 nm). The other sort of bismuth has six oxygen neighbors at the corners of a distorted octahedron (lengths of Bi–O bonds are placed between 0.21 and 0.28 nm) (7, 8). An intense broad band consisting of six components was reported between 595 and 380 cm^{-1} in the IR spectrum of α-Bi_2O_3 (9). Because of compounds containing Bi_2O_3 have similar IR spectra in this region, it was concluded that these bands are predominantly connected to the stretching modes of bismuth–oxygen framework (9, 10). In sillenites for instance the frequencies of asymmetric stretching modes of Bi–O bonds were observed in the range of 620–450 cm^{-1}. The relation between the frequencies of the four modes and the Bi–O bond lengths was found to be approximately linear for sillenites and nonlinear for α-Bi_2O_3.

The α-TeO_2 crystallizes in distorted rutile structure. Tellurium has distorted trigonal bipyramidal fourfold coordination by oxygen with two equatorial (0.1878 nm) and two axial bonds (0.2122 nm) (11, 12). In the IR spectrum of paratellurite two intense bands were observed at 675 and 780 cm^{-1}, having two shoulders (635, 714 cm^{-1}) at the first band (13). The four bands correspond to the stretching modes of the equatorial and axial bonds: $v^s_{eq} > v^{as}_{eq} > v^{as}_{ax} > v^s_{ax}$. The α-TeO_2 is built up by TeO_4 groups. However,

TABLE 1
Lattice Types and Space Groups

α-Bi_2O_3	α-$Bi_2Te_4O_{11}$	δ-Bi_2O_3	β-$Bi_2Te_4O_{11}$	$Bi_2Te_2O_7$	Bi_2TeO_5	α-TeO_2
(7, 8, 16)	(3, 17, 18)	(7, 16)	(3, 18)	(19)	(4, 20)	(11, 12)
Monoclinic	Monoclinic	Cubic	Cubic	Orthorhombic	Orthorhombic	Tetragonal
$P2_1/c$	$P2_1/n$	$Fm3m$	$Fm3m$	$Pcnb$	$Abm2$	$P4_12_12$

some tellurites contain TeO_3 polyhedra in trigonal–pyramidal configuration with equal lengths of Te-O bonds. Two bands of symmetric and degenerate TeO_3 modes ($v_{TeO_3}^s$ and $v_{TeO_3}^d$) were observed in the IR spectra of these tellurites. In certain tellurites the bands split as a consequence of symmetry loss in the TeO_3 group (13).

IR spectra of Bi_2TeO_5 have been published by Földvári et al. (14). They investigated single crystal samples with thicknesses of 0.095 and 16 mm in the ranges of 1600–850 and 2000–1600 cm^{-1}, respectively, at RT and 10 K. Kucha et al. (15) also published absorption spectra of Bi_2TeO_5 on single crystal samples of 0.43 and 1.3 mm thickness in the ranges of 2200–400 and 4000–2000 cm^{-1} and found at about 40 absorption bands. The bands at 425, 465, 500, 540, 570, and 610 cm^{-1} were assigned to the vibrations of Bi–O bonds. The bands at 670 and 705 cm^{-1} were assumed to belong to the Te–O bond. The bands at higher frequencies were assigned to the second harmonics and combinations of the low frequency bands.

In this paper we present IR absorption spectra of powdered α-Bi_2O_3, α-TeO_2, α-$Bi_2Te_4O_{11}$, β-$Bi_2Te_4O_{11}$, $Bi_2Te_2O_7$, and Bi_2TeO_5. For convenience the available literature data on lattice types, space groups, and interatomic distances are given in Tables 1–3.

EXPERIMENTAL

Bismuth oxide (Bi_2O_3) from Johnson Matthey (Grade 1) and tellurium oxide (TeO_2) prepared from tellur (99.999%) by oxidation with double destilled HNO_3 (Carlo Erba for

analysis) were used as starting materials. These materials were heated up to 450°C in air and after cooling they were ground and sieved. Powders with less than 63 μm particle size were used for the synthesis. Bi_2TeO_5 (a), $Bi_2Te_2O_7$ (b), β-$Bi_2Te_4O_{11}$ (c), and α-$Bi_2Te_4O_{11}$ (d) were prepared by the following procedures:

(a) Bi_2O_3 and TeO_2 powders were mixed in the ratio of 1 : 1 and fired at 850°C for 120 min under argon atmosphere in a platinum crucible.

(b) Bi_2O_3 and TeO_2 powders in the ratio of 1 : 2 were treated exactly in the same way, but the firing temperature was 700°C.

(c) Bi_2O_3 and TeO_2 powders in the ratio of 1 : 4 were treated as previous samples, except the firing was employed at 650°C for 30 min.

(d) β-$Bi_2Te_4O_{11}$ was annealed at 520°C under argon atmosphere for 10 min.

The composition of the samples was checked by X-ray diffraction using a Philips PW 1730 X-ray generator with Cu$K\alpha$ source. For IR measurements pellets were prepared by mixing the investigated compounds with KBr. The IR spectra were taken by a JASCO FT/IR-300E spectrometer at room temperature. The absorption bands were studied in the range of 1000–400 cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of β-$Bi_2Te_4O_{11}$, $Bi_2Te_2O_7$, α-$Bi_2Te_4O_{11}$, Bi_2TeO_5, α-Bi_2O_3, and α-TeO_2. Vibrational frequencies of the stretching modes of Te–O and Bi–O

TABLE 2
Interatomic Te–O Distances (nm) in Tellurites

α-$Bi_2Te_4O_{11}$ (17)				Bi_2TeO_5 (20)
Te1–O	Te2–O	Te3–O	Te4–O	Te–O
0.187	0.187	0.187	0.187	0.176
0.188	0.190	0.190	0.189	0.186
0.193	0.197	0.207	0.196	0.195
0.271	0.25	0.228	0.241	0.307
0.296	0.274	0.277	0.295	0.324
0.298	0.298	0.328	0.299	
0.343	0.301	0.336	0.322	
	0.343			

TABLE 3
Interatomic Bi–O Distances (nm) in Tellurites

α-$Bi_2Te_4O_{11}$ (17)		Bi_2TeO_5 (20)		
Bi1–O	Bi2–O	Bi1–O	Bi2–O	Bi3–O
0.220	0.222	0.210	0.219	0.196
0.224	0.233	0.231	0.227	0.205
0.231	0.235	0.231	0.227	0.205
0.239	0.240	0.244	0.242	0.286
0.250	0.247	0.261	0.242	0.286
0.278	0.267	0.268	0.302	0.305
0.279	0.284	0.304	0.302	0.305
	0.293	0.305		
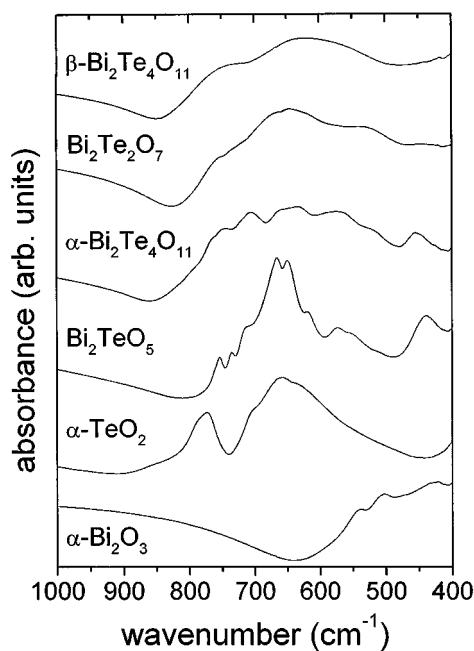
FIG. 1. Absorption spectra of bismuth tellurites, TeO$_2$, and α-Bi$_2$O$_3$.

Bi$_2$Te$_4$O$_{11}$ and Bi$_2$Te$_2$O$_7$ in peak positions and shape. They have strong overlapping peaks.

β-Bi$_2$Te$_4$O$_{11}$

In the spectrum of β-Bi$_2$Te$_4$O$_{11}$ symmetric and degenerate TeO$_3$ modes of the Te–O bonds can be found at $v^s_{TeO_3} = 765$ cm^{-1} and $v^d_{TeO_3} = 627$ cm^{-1}. Overlapping bands in the 600 to 400 cm^{-1} wavenumber range correspond to the asymmetric stretching mode of the Bi–O bond. Since no Bi–O bond lengths are available, no relation between the bond lengths and vibrational frequency can be established.

Bi$_2$Te$_2$O$_7$

In the spectrum of Bi$_2$Te$_2$O$_7$ a splitting of the vibrations of degenerate TeO$_3$ modes was observed ($v_{TeO1} = 757$ cm^{-1}, $v_{TeO2} = 670$ cm^{-1} and $v_{TeO3} = 647$ cm^{-1}) suggesting that the TeO$_3$ group has lower symmetry in Bi$_2$Te$_2$O$_7$ than in β-Bi$_2$Te$_4$O$_{11}$. Several overlapping bands can be detected in the range of low frequencies. Similarly to β-Bi$_2$Te$_4$O$_{11}$, no assignable interatomic Bi–O distances are available.

α-Bi$_2$Te$_4$O$_{11}$

In the region of 800–620 cm^{-1} there is a new band in the spectrum of α-Bi$_2$Te$_4$O$_{11}$ compared to that of Bi$_2$Te$_2$O$_7$. It is assumed that a Te$_2$O$_5$ group is formed from two TeO$_3$ polyhedra sharing an oxygen. Four stretching modes of the Te–O bonds appear. We assign two of them to TeO$_2$ groups and the two others to the Te–O–Te bridge, similarly to the compounds MgTe$_2$O$_5$ (13, 21) and Te$_2$V$_2$O$_9$ (13, 22). The vibrational frequencies are $v^s_{TeO_2} = 749$ cm^{-1}, $v^{as}_{TeO_2} = 706$ cm^{-1}, $v^{as}_{Te-O-Te} = 667$ cm^{-1}, and $v^s_{Te-O-Te} = 631$ cm^{-1}. This result is consistent with Refs. (17, 18), where it was established that the structure of α-Bi$_2$Te$_4$O$_{11}$ consisted of an ordered intergrowth of fluorite Bi$_2$Te$_2$O$_7$ and rutile or

bonds in various bismuth tellurites are summarized in Table 4. The band positions were determined by the help of the second derivatives of the spectra. Four bands can be seen in the IR spectrum of our α-TeO$_2$ sample in Fig. 1 at 770, 708, 666, and 632 cm^{-1}. These bands, however, are shifted by 5–10 cm^{-1} toward lower frequencies as compared to Ref. (13). Spectra of bismuth tellurium oxides are similar to each other, but differ from the spectrum of TeO$_2$ because their structures consist of TeO$_3$ groups. IR spectra of bismuth tellurites generated by TeO$_3$ groups can be characterized by two vibrations of symmetric and degenerate TeO$_3$ modes of the Te–O bonds. The two ranges are 765–730 and 670–630 cm^{-1}, respectively. Splitting of these bands is observed in the case of Bi$_2$Te$_2$O$_7$, α-Bi$_2$Te$_4$O$_{11}$, and Bi$_2$TeO$_5$ due to decrease in the symmetry of TeO$_3$ group. In Fig. 1 one can observe the similarity between the spectra of β-

TABLE 4
Vibrational Frequencies of the Stretching Modes of Te–O and Bi–O Bonds in Bismuth Tellurites

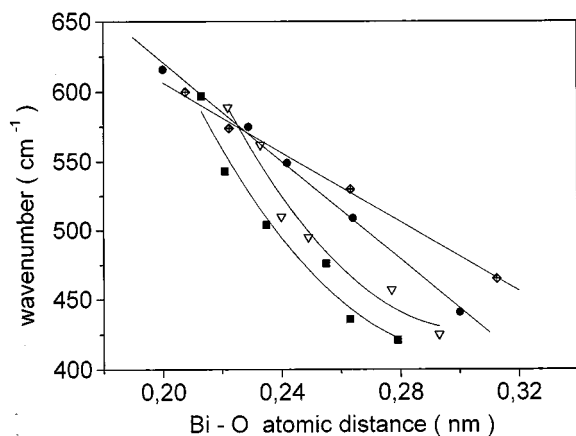| Compounds	Vibrations of Te–O bonds (cm^{-1})					Vibrations of Bi–O bonds (cm^{-1})					
β-Bi$_2$Te$_4$O$_{11}$	765				627						419
Bi$_2$Te$_2$O$_7$	757			670	647				528	450	427
α-Bi$_2$Te$_4$O$_{11}$	749		706	667	631	589	562	510	495	457	425
Bi$_2$TeO$_5$	755	737	716	667	647	616	575	549	509	441	
α-Bi$_2$O$_3$						597	543	504	476	436	421
TeO$_2$	770	708	666	632							

FIG. 2. Relation between vibrational frequencies and groups of Bi–O bond lengths in bismuth tellurites. α-Bi_2O_3 (squares), α-$Bi_2Te_4O_{11}$ (triangles), Bi_2TeO_5 (circles), and $Bi_{12}GeO_{20}$ (diamonds). $Bi_{12}GeO_{20}$ data are reproduced from R. J. Betsch and W. B. White, *Spectrochim. Acta A* **34**, 505 copyright 1977, with permission from Elsevier Science.

fluorite TeO_2 slabs containing

$$
\begin{array}{ccc}
O & & O \\
\diagdown & & \diagup \\
& Te\text{-}O\text{-}Te & \\
\diagup & & \diagdown \\
O & & O
\end{array}
$$
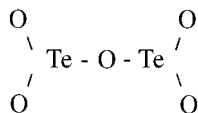
subunits. Six asymmetric stretching modes of Bi–O bonds are at 589, 562, 510, 495, 457, and 425 cm^{-1}. These six vibrational frequencies correspond to six groups of bond lengths. The group can be defined as an average value of bond lengths differing by less than 0.013 nm. The relation between the vibrational frequencies and groups of Bi–O bond lengths is shown in Fig. 2. This relation is found, similarly to the case of α-Bi_2O_3, to be nonlinear.

Bi_2TeO_5

The largest number of bands were observed in the spectrum of Bi_2TeO_5. The five highest energy bands belong to Te–O bonds. From the biggest splitting of the degenerate TeO_3 mode the largest deformation of the TeO_3 polyhedra can be concluded. The difference (0.02 nm) between the three shortest Te–O bonds is the biggest in our investigated bismuth tellurites. This value is rather high even in comparison with other tellurites containing tellurium atoms with threefold coordination. In the range of low frequencies there are five asymmetric stretching modes of the Bi–O framework at 616, 575, 549, 509, and 441 cm^{-1}. Comparing our spectrum with that of Kucha *et al.* (15) there are differences in both the region of 1000–620 cm^{-1} and the region of 620–400 cm^{-1}. In the present work we used sintered powders of stoichiometric Bi_2TeO_5, while Kucha *et al.* used

single crystal samples. Földvári *et al.* (14) have reported on the strong nonstoichiometric character of the Bi_2TeO_5 crystal. In Fig. 2 the relation between the frequencies of asymmetric stretching modes and groups of Bi–O bond lengths in Bi_2TeO_5 is shown. The dependence for Bi_2TeO_5 is linear, as seen in sillenites (9) and in contrast to that seen in α-$Bi_2Te_4O_{11}$ and α-Bi_2O_3. This fact can be interpreted on a structural basis. In Bi_2TeO_5 the Bi2–O and Bi3–O polyhedra look very similar to the Bi–O polyhedron sillenites having Bi–O of bond lengths in three equal pairs and one short bond. Among the three pairs the two shortest are in the same plane in both compounds. The short bond and the long pair are located on the opposite side of this plane. In α-$Bi_2Te_4O_{11}$, however, the Bi–O polyhedra are more complex, as seen in the highly distorted octahedra of α-Bi_2O_3.

CONCLUSION

In this paper infrared spectra of α-$Bi_2Te_4O_{11}$, β-$Bi_2Te_4O_{11}$, $Bi_2Te_2O_7$, and Bi_2TeO_5 have been compared and analyzed. Absorption bands were studied in the range of 1000–400 cm^{-1}. Bands in the region of 620–400 cm^{-1} correspond to the stretching modes of the bismuth–oxygen framework, while those in the region of 800–620 cm^{-1} belong to stretching vibrations of the Te–O bonds. Tellurites contain trigonal–pyramidal configuration of TeO_3 polyhedra with equal bond lengths (within 0.02 nm). Similarity can be observed between the IR spectra of β-$Bi_2Te_4O_{11}$ and $Bi_2Te_2O_7$. Te_2O_5 groups are formed by connected TeO_3 polyhedra in α-$Bi_2Te_4O_{11}$. Largest deformation of the TeO_3 polyhedra can be concluded in Bi_2TeO_5. The difference between its three shortest Te–O bond lengths is the biggest among the investigated bismuth tellurites and moreover this value is rather high even in comparison with other tellurites containing tellurium atoms with threefold coordination. The relation between the observed IR bands and the Bi–O bond lengths has been found to be nonlinear for α-Bi_2O_3 and α-$Bi_2Te_4O_{11}$ and linear for Bi_2TeO_5.

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