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Crystal structure, Raman spectrum and lattice dynamics of a new metastable form of tellurium dioxide: γ -TeO₂

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Abstract

The crystal structure of a new metastable form of tellurium dioxide, γ -TeO₂ (orthorhombic, $P2_12_12_1$ (no. 18); a = 4.898 Å, b = 8.576 Å, c = 4.351 Å; Z = 4) was solved ab initio and refined to $R_B = 0.0387$ and $R_p = 0.115$, on the basis of a Rietveld analysis of its powder X-ray diffraction pattern. Each Te atom is coordinated to four oxygen atoms, and its coordination polyhedron has a view of distorted trigonal bipyramid (disphenoid) TeO₄E with one equatorial corner occupied by lone pair E. These units frame a three-dimensional network of the same type as the α -TeO₂ one. There exist two different kinds of Te–O–Te bridges in γ -TeO₂; one of them is nearly symmetric, and the other is highly asymmetric. The former bridges constitute polymeric chains along the Oz-axis.

Such a characterization of the γ -TeO₂ structure is supported by the analysis of the Raman spectra using the lattice dynamical model treatment in which the lattice vibrations are considered jointly with the elastic properties. All the longwave frequencies and the elastic constants were thus estimated. Possible relations between the structure of the TeO₂ glass and the γ -phase are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Tellurium dioxide TeO_2 belongs to the category of compounds in which all the atoms are the so-called p-elements, having non-bonding valence electron pairs (lone pairs E). For such compounds, in their solid phases, the stereochemical effect of the lone pairs results in a strong asymmetry of the coordination polyhedra of the constitutive p-elements. Actually those polyhedra can be regarded as consisting of two demi-spheres of different radii. Demi-sphere I contains active valence electrons which form (relatively short) chemical bonds with the nearest neighbours situated on the one side of the p-element. Demi-sphere II, situated on the other side, contains the inert electron cloud surrounded by more distant neighbours weakly interacting with it.

contain cavities, tunnels or planes in which the lone pairs E are located and interact. Their lattices, as a rule, are microscopically labile, macroscopically compliant and predisposed to polymorphism. Many of them, like TeO₂, and almost all the Te^{IV} containing compounds (including the glasses), exhibit remarkable properties related to macroscopic polarization and polarisability (dielectric, piezoelectric, optic, electro-acoustic) which are of great interest for fundamental science and technology. The origin of such properties, particularly for TeO₂-based glasses, is not yet clearly identified, but it can be thought that it is surely related to the peculiarities of the electron distribution inside the coordination polyhedra. Therefore the detailed knowledge of the atomic arrangement in those polyhedra is of prime importance.

The crystals built up from such structural units therefore

In discussing the structure of TeO₂-based glasses, which are promising materials for use in optical fibre or in non-linear optical devices [1], the two well-known crystalline ambient-pressure polymorphs of tellurium

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Fig. 1. The disphenoid as a basic structural unit of the α - and β -TeO₂ crystal structures (the arrows visualize the direction toward which points the lone pair E of the Te atom).

dioxide, α -TeO₂ paratellurite [2,3], and β -TeO₂ tellurite [4], are usually referred to as the virtual parents. In both polymorphs, the oxygen environment of Te atoms corresponds to a highly distorted TeO₆ octahedron. Its demi-sphere I contains four oxygen atoms forming two strong (largely covalent) short equatorial bonds (Te–O_{eq}), and two much weaker, and therefore longer, axial bonds (Te–O_{ax}). Demisphere II contains two Te···O non-bonding contacts and the lone pair E.

Customarily, the TeO_4 disphenoids corresponding to demi-sphere I (Fig. 1) are considered as the basic structural units which build up:

- either the three-dimensional network of α-TeO₂, by sharing the O corners (via simple Te-_{eq}O_{ax}-Te bridges);
- or the two-dimensional framework of β-TeO₂, by sharing alternately the O corners and the O–O edges (double bridge

$$\begin{array}{c} ax \quad \mathbf{O} \quad eq \\ Te \swarrow \mathbf{O} \swarrow Te \\ eq \\ \mathbf{O} \checkmark ax \end{array}$$

Consequently, the crystal chemistry of TeO_2 -rich crystalline compounds or glasses are usually discussed within the frame of this idea.

However, such an opinion is not unique. Some authors consider TeO₂ crystals as molecular structures (see Ref. [3] and references therein). In our recent treatment of the vibrational properties of α - and β -TeO₂ [5], we have found spectrochemical arguments supporting this point of view. It could be concluded that the electron cloud inside the asymmetric Te-_{eq}O_{ax}-Te bridges is so disbalanced that the vibrating lattices behave rather as molecular structures consisting of the isolated TeO_{2eq} entities, than a framework of polymerized Te-O-Te bridges. These arguments are

 Table 1

 Conditions of data collection and profile refinement (esd's are given in parentheses)

Lattice parameters (Å)	a = 4.898(3), b = 8.576(4)
	c = 4.351(2)
Volume (Å ³)	182.76(2)
$\rho_{\rm exp} ({\rm g}{\rm cm}^{-3}), \rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	5.80(5), 5.85
Ζ	4
Space group	$P2_12_12_1$ (no. 18)
Wavelength (Å)	1.540598
2θ range (°)	20-100
Step range (°)	0.04
Counting time (s)	75
Zero shift (°)	-0.017(1)
Number of reflections	258
Number of parameters	21
Scale	$0.319(3) \times 10^{-3}$
Refinement program	Fullprof [10]
Profile function	Pseudo-Voigt
Profile parameters	V = 0.21(3); V = 0.06(2)
	$W = 0.003(4); \ \eta = 0.77(1)$
Reliability factors ^a (%)	$R_{\rm bragg} = 3.87; R_{\rm p} = 11.5;$
	$R_{\rm wp} = 12.6$
^a $R_{\text{bragg}} = 100 \sum I_i - I_{ci} / \sum I_i ;$	$R_{\rm p} = 100 \sum Y_i - Y_{ci} / \sum Y_i $

 $R_{\rm wp} = 100 [\sum W_i / |Y_i - Y_{ci}|^2 / [\sum w_i / |Y_i|^2]^{1/2}.$

reinforced by the Raman spectrum behaviour during hydrostatic compression of α -TeO₂ [6], which clearly indicates (as previously shown by a powder diffraction study [2]) an evolution of the crystal structure toward a framework.

Now, an interesting question arises: can polymerized TeO₂ lattice exist under ambient conditions? In this article we present the detailed structural and spectroscopic (Raman diffusion) data on a new crystalline form of tellurium dioxide (that we have called γ -TeO₂) which, in our opinion, positively answer this question. These data are analysed jointly with the results of the lattice-dynamical model treatment, which provides an interpretation of the crystal vibrations and clarifies their connection with the structural peculiarities.

2. Experimental techniques

More or less well-crystallized γ -TeO₂ is obtainable when pure TeO₂ glass, or TeO₂-rich glasses containing 5–10 mol% of oxides like WO₃ [7], Nb₂O₅ [8] or PbO [9], are recrystallized at low temperatures. Well crystallized and practically pure γ -TeO₂, (small amounts of α -TeO₂ and of the residual TeO₂-rich glass were detected on the X-ray diffraction (XRD) pattern) was prepared by slowly heating up to 440°C, and then annealing for 60 h at the same temperature, a glassy sample containing 5 mol% of Nb₂O₅.

The XRD pattern used for the ab initio crystal structure determination was recorded on a D5000-Siemens diffractometer (Bragg–Brentano configuration) equipped with a back monochromator, under the conditions reported in



Fig. 2. Powder Raman spectra of the γ -TeO₂ crystallized from TeO₂ glasses doped with oxides: (a) WO₃; (b) Nb₂O₅; (c) PbO.

Table 1. Changing the way of dusting the holder with the sample holder did not result in significant changes of the relative intensities of the diffraction lines, so indicating that no orientation effects were occurring.

The individual structure factors were extracted from the pattern by a "pattern matching procedure" using the FULL-PROF Rietveld program [10]. Then the SHELXS 90 and SHELXL 97 [11,12] programs were used for the structure determination. The scattering factors were those of the International Tables for X-ray Crystallography [13]. They were corrected for anomalous diffusion effects.

Raman spectra of all the samples were recorded in the $20-1200 \text{ cm}^{-1}$ range using a Dilor spectrometer (XY model) equipped with a CCD detector and an Ar⁺ laser (514.5 nm exciting line) in a backscattering geometry. Fig. 2 exhibits the spectra of γ -TeO₂ synthesized from TeO₂-rich glasses containing different dopings, WO₃ (5%), NbO_{2.5} (10%) and PbO (5%). The shapes of these spectra are close, but that related to the lattice doped by PbO is more refined. Therefore, it will be referred throughout this paper. For comparison, the Raman spectra of α -, β - and γ -TeO₂ as well as the spectrum of the glass, are jointly presented in Fig.3.

3. Structure

The XRD pattern (Fig. 4) has been indexed (Table 2) in the orthorhombic system (space group $P2_12_12_1$; unit cell para-

meters: a = 4.893(3) Å, b = 8.576(4) Å, c = 4.351(2) Å) with the help of the ITO automatic indexing program [14]. The density measured ($d_{exp} = 5.80(5)$ g cm⁻³) implies Z = 4 TeO₂ per unit cell ($d_{calc} = 5.85$ g cm⁻³). These values are not contradictory with (but are more accurate than) the previously published ones [7] which corresponded to a less well-crystallized sample obtained from a pure TeO₂ glass. The coordinates of atomic positions are given in Table 3, and some characteristics of the atomic arrangement in the γ -TeO₂ lattice are presented in Table 4.

The environment of tellurium atom is shown in Fig. 5. Formally, it is coordinated to six oxygen atoms forming a highly distorted octahedron involving four oxygen atoms separated from Te by an interval of about 1.85-2.20 Å, and two distant oxygen atoms, separated by 2.69 and 3.16 Å. If the latter atoms are excluded, the typical disphenoid TeO₄E becomes appropriate, in which the lone pair constitutes the third equatorial vertex of the trigonal bipyramid. It is worth noting that one of the two *axial* bonds (Te-O(1)¹ = 2.20 Å) is much longer than the other one (Te-O(2)¹ = 2.02 Å). By sharing O(1) and O(2) corners, the TeO₄E units frame the three-dimensional network visualized in Fig. 6a. Such a network makes room for wide rectangular tunnels containing the lone pairs of tellurium atoms.

The shortest three bonds, namely, the two equatorial ones, Te-O(1) and Te-O(2), and the shortest axial one, $Te-O(2)^{1}$, can be regarded as constituting the helical



Fig. 3. Raman spectra of various phases of TeO₂: (a) α -TeO₂; (b) β -TeO₂; (c) γ -TeO₂; (d) glassy TeO₂.

chains of corner-sharing TeO₃ pyramids (TeO₃E tetrahedra) displayed in Fig. 6a. Two of those chains, developed around the 2_1 screw axes along the Oz direction, are shown in Fig. 7a.

A comparison of the structure of γ -TeO₂ with that of paratellurite, α -TeO₂ (space group *P*4₁2₁2) [2,3], reveals a general analogy (Figs. 6 and 7) in their constitutions. Actu-

ally, both structures are built up from similar basic units interconnected in the same way, e.g. via the $Te_{-eq}O_{ax}$ -Te simple bridges. However, α -TeO₂ contains a single set of such bridges which are essentially asymmetric (1.87–2.12 Å) and which constitute a regular three-dimensional network (Fig. 6b), whereas in γ -TeO₂, the TeO₄E units are alternately linked by nearly symmetric (1.95–2.02 Å) and



Fig. 4. Observed (...), calculated (—) and difference (below) X-ray powder patterns for γ -TeO₂. Vertical bars indicate the reflection positions for γ -TeO₂ (upper bars) and for α -TeO₂ (lower bars).

Table 2 X-ray powder data for $\gamma\text{-}TeO_2$

h,k,l	$d_{\rm obs}({\rm \AA})$	d_{calc} (Å)	$I/I_{\rm max}$ (%)	h,k,l	$d_{\rm obs}$ (Å)	d_{calc} (Å)	<i>I</i> / <i>I</i> _{max} (%)
020	4.30	4.29	2	141	1.7925	1.7902	11
110	4.26	4.25	8	032	1.7278	1.7311	< 1
011	3.884	3.880	31	231	1.7122	1.7102	9
101	3.255	3.253	41	132	1.6330	1.6322	14
120	3.230	3.226	100	240	1.6147	1.6132	6
021	3.047	3.054	55	310	1.5989	1.6039	9
111		3.041		212		1.5979	
121	2.597	2.591	3	301	1.5301	1.5287	3
200	2.451	2.449	8	320	1.5262	1.5259	2
031	2.392	2.389	10	151	1.5171	1.5172	7
210	2.355	2.355	3	142	1.4548	1.4578	< 1
0 0 2	2.177	2.175	2	321	1.4384	1.4399	< 1
131	2.149	2.147	7	013	1.4328	1.4299	1
040		2.144		060	1.4267	1.4293	2
201	2.130	2.134	2	232	1.4119	1.4136	1
220		2.127		103	1.3914	1.3905	2
012	2.110	2.109	13	113	1.3726	1.3726	5
211	2.073	2.071	4	160		1.3721	
102	1.9877	1.9881	2	061	1.3588	1.3579	1
140	1.9651	1.9641	6	331	1.3477	1.3480	5
022	1.9381	1.9399	13	052		1.3469	
112		1.9367		251	1.3380	1.3370	1
221	1.9128	1.9106	16	161	1.3091	1.3086	2
230	1.8622	1.8599	3	242	1.2948	1.2958	2
122	1.8031	1.8036	< 1	033		1.2933	
				312		1.2910	

Table	3						
Final	atomic	coordinates	and	isotropic	thermal	coefficients	for
atoms	in γ-Te	O2 (esd's are	e in p	arentheses	s)		

Atom	Site	x	у	z	$B(\text{\AA}^2)$
Те	4a	0.9696(4)	0.1016(2)	0.1358(4)	0.17(3)
O(1)	4a	0.759(3)	0.281(2)	0.173(4)	4.0(4)
O(2)	4a	0.855(3)	0.036(2)	0.727(3)	4.3(4)

highly asymmetric (1.86-2.20 Å) bridges, thus forming a lattice in which the above mentioned chains can be clearly identified.

4. Raman spectrum and lattice dynamics

The primitive cell of γ -TeO₂ contains 12 atoms, and the 33 longwave lattice vibrations are distributed between the

Table 4

Main interatomic distances (A),	angles (°), symmetry	y operations and bond	valences in γ-TeC	D_2 (esd's are	given in parentheses)

Те	O(1)	O(1)1	O(1)2	O(2)	O(2)1	O(2)2	$ u_{ij}$	Symmetry
O(1)	1.86(2)	2.93(2)	4.94(2)	2.90(2)	2.79(2)	3.23(2)	1.38	
O(1)1	91.9(5)	2.20(2)	4.34(2)	2.56(2)	4.11(2)	4.66(2)	0.54	x, y, 1 + z
O(1)2	158.2(6)	106.7(6)	3.16(2)	3.89(2)	3.34(2)	3.38(2)	0.04	x, -y, 0.5 + z
O(2)	99.2(4)	76.1(4)	96.3(5)	1.94(1)	2.48(2)	4.35(2)	1.09	
O(2)1	91.8(5)	153.6(5)	76.7(4)	77.6(5)	2.02(2)	2.48(2)	0.88	1 - x, 0.5 + y, z
O(2)2	88.3(5)	144.5(6)	85.3(4)	138.8(6)	61.7(5)	2.69(1)	0.14	0.5 + x, 0.5 - y, -z
$\sum \nu_{ij}$							4.07	



Fig. 5. Anionic coordination around the tellurium atoms. The arrow indicates the direction toward which the lone pair E points.

symmetry species as follows:

 $9A_1 + 8A_2 + 8B_1 + 8B_2$

All of them are Raman active. The eight modes corresponding to the vibrations of the eight shortest (equatorial) Te–O bonds can be expected in the interval 500-850 cm⁻¹ which is the region of the stretching modes of the TeO₂ lattices [5]. Only four of those, near 611, 683, 752 and 819 cm⁻¹ are seen well in the experimental spectra, and a weak band near 645 cm^{-1} can be added to them (Fig. 2). The existence of one high-frequency strong band dominating the *stretching* region is typical for the Raman spectra of TeO₂ polymorphs [5]. The particular feature of the spectra in Fig. 2 is the very high intensity of the band near 426 cm⁻¹. Qualitatively, the origin of these two intense bands has been already discussed in Ref. [5].

To better clarify the relationships between the crystal structure and the Raman spectrum under considerations, the lattice-dynamical treatment of γ -TeO₂ was performed by using the above structural data and the modified valence force field model recently elaborated for α - and β -TeO₂ lattices [5]. Within this model, the short-range Te-O and O–O interactions up to distances L = 3.5 Å were taken into account. They were characterized by two-body force constants K_{Te-O} and K_{O-O} evaluated from the empirical $K_{\text{Te}-O}/L_{\text{Te}-O}$ and K_{O-O}/L_{O-O} dependences empirically found in Ref. [5]. To these parameters, the three-body force constants of the O-Te-O and Te-O-Te angles were added jointly with the non-diagonal Te-O/Te-O parameters describing the interactions between two adjusted Te-O bonds via Te and O atoms. The corresponding values were transferred from Ref. [5].

Among the calculated results, the main attention was paid to the Raman active modes (frequencies and eigenvectors) and to the elastic properties of the lattice. Some of these results are presented in Table 5.



Fig. 6. Stereoview of the 3D network of corner-sharing TeO_4E units in (a) γ -TeO₂ and (b) α -TeO₂ for comparison (the symbols for O(1) and O(2) atoms are the same as in Fig. 5). In (a), the broken lines visualize the longer Te–O(1) bonds which individualize the polymeric chains parallel to Oz (shadowed zones).



Fig. 7. Spatial view of the two polymeric chains underlined (shadowed zones) in Fig. 6 in (a) γ -TeO₂ (real chains) and (b) α -TeO₂ (virtual chains).

5. Discussion

The present analysis of the structure and the Raman spectrum of γ -TeO₂ is mainly aimed at understanding the peculiarities of the interatomic bonding in this lattice, and their spectrochemical manifestations. To compare our results with the properties of the known TeO₂ structures, it is necessary to take into account the data on an isolated TeO₂ molecule [15], as well as the previous considerations of the lattice dynamics of α - and β -TeO₂ [5].

In gaseous state, TeO₂ exists as three-atomic polar molecules ($C_{2\nu}$) in which the double Te=O bonds (L = 1.83 Å) form an angle of 110° [15]. It can be thought

Table 5

Calculated frequencies (cm⁻¹), elastic constants C_{ij} (GPa) and the bulk modulus *B* (GPa) of the γ -TeO₂ lattice. The frequencies in brackets show the positions of the observed vibrations to which the calculated ones are attributed

A_1	A_2	B_1	B_2	Elastic characteristics
56 (66)				<i>C</i> ₁₁ 29.6
104 (77?)	108	83 (77?)	95	C ₂₂ 39.8
119 (116)	127	121	131	C_{33} 67.0
156 (140)	177 (174)	193	159	C_{12} 21.7
241 (226)	264	231	223	C_{13} 7.7
311 (307)	309 (291)	341	315	C_{23} 2.3
419 (426)	438	430	442	C_{44} 28.6
622 (611)	614 (645)	701	701	C ₅₅ 11.6
702 (683)	752 (752)	806 (812)	758	C_{66} 24.1
				B 21.7

that the spatial arrangement of the molecules during their condensation into a solid phase would be primarily governed by electrostatic interactions. Actually, a negative (oxygen) anion of any molecule would approach a positive (tellurium) cation of another molecule. It is highly likely that the way going via tellurium perpendicularly to the TeO₂ plane is the most probable: along this line, the electron screening of the Te(++)–O(-) attraction is the smallest. Two oxygen atoms can symmetrically approach any Te atom along this line, thus forming the two (largely ionic) Te–O_{ax} bonds with the relevant O–Te–O angle close to 180°.

Thus, in solid TeO₂, the four oxygen atoms are present in the demi-sphere I of Te atom; jointly with the E pair, they constitute the TeO₄E disphenoid. However, the electron distribution among the four relevant Te–O contacts is essentially anisotropic in accordance with their nature. The two shortest Te–O_{eq} ones evidently correspond to the initial Te=O covalent bonds of the molecule; their lengths, as a rule, lie in interval 1.85–1.95 Å, and they form an angle $O_{-eq}Te_{eq}$ –O of about 100°. The two Te–O_{ax} contacts have lengths in interval of about 2.05–2.20 Å and form an angle close to linear, thus manifesting their ionic nature. Demisphere II includes two O atoms separated from Te by about 2.7–3.2 Å and, in fact, it is a part of a spatial cavity serving as a storage of the E-pairs.

The recent quantum mechanical ab initio calculations of the cluster-like fragments of the α -TeO₂ lattice estimate the bond orders of the Te–O contacts as follows: 1.7 (1.87 Å), 0.3 (2.12 Å), and ~0 (2.9 Å) [16]. This is in line with the results of our lattice-dynamical study of α - and β -TeO₂ [5]. In analysing the energetics of the atomic motions in these two lattices, it was found that: (i) The high-frequency vibrations ($\omega > 500 \text{ cm}^{-1}$) represent the *intramolecular* Te–O_{eq} stretching motions; the number of those vibrations always corresponds to the number of Te-O_{eq} bonds; (ii) Among the Raman-active stretching vibrations, there is always one with very high intensity which dominates all the spectra. This is absolutely opposite to the view of the Raman spectra of typical "homogeneous" framework-like XO₂ structures built up from symmetric X-O-X bridges (see, e.g. Raman spectra of silica [15]). In such structures, the high-frequency region of the spectra consists of the stretching asymmetrical vibrations ν_{asym} of the X–O–X bridges. Therefore, they would necessarily have low Raman-intensity, which is dictated by asymmetrical bond length changes (within the bridges) inherent for these vibrations; (iii) The Te-Oax potentials (jointly with O-O ones) dominate the frequency interval below 400 cm⁻¹, thus describing the intermolecular forces.

The discussed properties manifest well a quasi-molecular character of the α and β -TeO₂ lattices [5], i.e. the essential anisotropy of the electron distribution in their TeO₄ groupings, or, in other words, the strong asymmetry of the chemical bonding in the Te–O–Te bridges.

Let us concentrate now on the data obtained for γ -TeO₂. In the light of the issue made above, the central attention must be paid to the point which differentiates this structure from the α - and β -TeO₂ ones. That is the existence of two types of Te–O–Te bridges in γ -TeO₂, respectively, less symmetric (we call it a-bridge) and much more symmetric (s-bridge) than the bridges in α - and β -TeO₂. In the a-bridge, the shortest Te– O_{eq} bond of 1.86 Å (close to that in the Te O_2 molecule), is alternated with a much longer Te...O axial contact (2.20 Å). In contrast to this, the characteristics of the s-bridge indicate much more isotropy in the Te-O bonding. This bridge is shorter than any other Te-O-Te bridge existing in the crystalline lattices of TeO₂ and tellurates [17]. The bond lengths (1.95 and 2.02 Å) are very close to their average magnitude, i.e. the bridge is almost "balanced".

In contrast to the Raman spectrum of α -TeO₂, which manifests the quasi-molecular character of this lattice [5], it is likely that the vibrational properties of γ -TeO₂ indicate the occurrence of the intermolecular bonding (polymerization) within the Te(1)-O(2)-Te(2)-O(2) chain (Fig. 7a). Let us consider the Raman spectrum of γ -TeO₂ (Fig. 2) and focus our attention on the six lines observable above 400 cm^{-1} : 426, 611, 645, 683, 752 and 812 cm⁻¹. The assignment of these lines to the calculated vibrations is given in Table 5. The analysis of their shapes (eigenvectors) leads us to the following issue: the lines near 426 and 611 cm⁻¹ correspond to the totally symmetric combinations (A₁ species) of the ν_{sym} and ν_{asym} stretching vibrations in the s-bridges, respectively; the line near 683 cm⁻¹ to the totally symmetric combination (A₁ species) of the ν_{asym} vibrations of the a-bridge. The weak lines near 645 and 752 cm^{-1} correspond to A₂-combinations of ν_{asym} of the s-bridges

and of ν_{asym} of the a-bridges, respectively, whereas the vibration near 820 cm⁻¹ (attributed to the B₁ species) is more delocalized.

The high intensity of the line near 683 cm^{-1} unambiguously indicates that, from the point of view of crystal chemistry, its description as ν_{asym} of the a-bridges is not adequate to "chemical reality". Actually, this is due to the totally symmetric pulsation of all the covalent Te-O_{ea} bonds (1.86 Å), that the line in question has such a high intensity (such a picture is characteristic for the strongest highfrequency vibrations in the Raman spectra of α - and β -TeO₂). Formally, those are the asymmetric vibrations ν_{asym} of the Te-_{eq}O_{ax}-Te bridges, but in reality the Te-Oeq bond contribution essentially predominates [5]. Moreover, the calculations show that no vibration can be specified as ν_{sym} of the a-bridge; so the term "a-bridge" has rather geometrical than chemical sense. In fact, it must be considered as the strong (largely covalent) Te-Oea bond (1.86 Å) adjusted with the weak electrostatic $Te-O_{ax}$ contact (2.20 A) interconnecting the above mentioned helical chains.

The two vibrations of the s-bridge demonstrate other situation: the line near 426 cm⁻¹ (ν_{sym}) is rather intense, whereas that near 611 cm⁻¹ (ν_{asym}) is much weaker. Thus this resembles the properties of X–O–X bridge vibrations in the Raman spectra of such typical ("homogeneous") XO₂ frameworks as various polymorphs of silica [18]. For example, the A₁-spectrum of α -quartz contains a very intense line near 464 cm⁻¹ and a weak line near 1080 cm⁻¹. Those lines are unambiguously attributable to ν_{sym} and to ν_{asym} of the Si–O–Si bridge, respectively [19]. According to our present treatment of the γ -TeO₂ spectrum, the two lines near 426 and 611 cm⁻¹ are the homologues of the two above mentioned lines of quartz, respectively.

Thus the spectrochemical properties indicate that a Te-axOeq-Te polymerization occurs in the s-bridges, and is practically absent in the a-bridges. At the same time, in extrapolating the above mentioned quantumchemical estimates [16] of the orders of the different tellurium-oxygen bonds, it can be thought that, in abridge, the order of the Te–O (1.86 A) bond is nearly 2, and that of the Te···O (2.20 Å) contact is about ten times lesser. At the same time, the orders of the bonds in the s-bridge are much closer to their average value of about 1. Consequently, the γ -TeO₂ lattice can be considered as a chain structure with well-pronounced covalent bonding along the z-axis, and with mainly ionic inter-chain interactions. In this case, the lattice can be compared with the chain structure of crystalline SeO_2 [20] (this latter compound is isovalent to TeO_2 , and, in a gaseous phase, also exists as an isolated three atomic molecule).

The calculated bulk modulus of γ -TeO₂ (Table 5), mainly determined by interactions of atoms separated by 2.5–3.3 Å, is found to be about two times lower as that of β -TeO₂ and three times lower than that of α -TeO₂.

6. Concluding remarks

From the crystal chemistry point of view, the main issue of the present analysis of the new γ -form of crystalline TeO₂ is that this material can exist under ambient condition as a system having a well-pronounced one-dimensional (intermolecular) polymerization. In jointly considering the properties of α -, β -, and γ -TeO₂, it can be concluded that the electron cloud within the TeO₄ grouping has a very variable character providing the polymorphism of the TeO₂ lattices.

Taking into account the high compressibilities of these lattices, it is likely that the structure and the potential function relief of any solid phase of TeO₂ has to be very sensitive to the increase of external pressure which would provoke a homogenization of the electron distribution, i.e. the Te $-O_{eq}$ -Te $-O_{ax}$ bond polymerization. Any solid phase of TeO₂ at ambient conditions (including the glass) can be regarded as an "incipient" framework which would develop at increasing pressure, in continuously changing the picture of the interatomic bonding and, most likely, the related properties, as for example, optic characteristics.

In comparing the Raman spectra of the TeO₂ glass with those of α -, β -, and γ -TeO₂ crystals, it can be observed (see Fig. 3), that the band centred near 430 cm^{-1} in the spectrum of the glass is essentially stronger than the line near 400 cm^{-1} of α -TeO₂, and then that at 440 cm^{-1} of β -TeO₂. Therefore, it can be thought that a considerable contribution to this band comes from ν_{sym} vibrations of symmetric Te-O-Te bridges resembling those present in the chains of γ -TeO₂; thus it appears that such chains represent one of main structural features of the TeO₂ glasses. If so, in the TeO2-glass Raman spectrum, the intensity of the band near 430 cm⁻¹ would increase under hydrostatic compression, whereas that of the band near 650 cm^{-1} would decrease. We believe that such an idea can be checked by studying the pressure-induced evolution of the relevant spectra, and hope that it can stimulate the experimental activity in this direction.

In summary, we present the detailed information on the structure of the new γ -phase of TeO₂, complemented by its Raman spectrum. By using these data, we carry out a lattice

dynamical treatment thus interpreting the lines in the spectrum. In analysing the results obtained, we find that the γ -TeO₂ lattice can be considered as a chain system. In discussing the Raman spectra of α -, β , γ lattices jointly with that of the TeO₂ glass, we venture the opinion that chain character of the structure is well pronounced in the glass.

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