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# Crystal structure and dynamical properties of a new tellurite: AgTITeO<sub>3</sub>

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## ABSTRACT

The structure of a newly synthesized AgTITeO<sub>3</sub> crystalline compound has been solved from single crystal X-ray diffraction data and refined to a final reliability factor R1 = 0.037. It was found having an orthorhombic lba2 space group symmetry with unit cell parameters a = 14.708(7) Å, b = 10.745(6) Å, c = 5.166(3) Å, Z = 8. Its lattice is divided into separated AgTITeO<sub>3</sub> sheets parallel to [0 1 0] which are formed by TeO<sub>3</sub> pyramids, TIO<sub>4</sub> disphenoids and AgO<sub>6</sub> octahedra sharing either corners or edges. At the same time, from the crystal chemistry point of view, it can be classified as a typical island-type compound made up from molecular-like [TeO<sub>3</sub>]<sup>2–</sup> ortho-anions weakly connected with Ag<sup>+</sup> and Tl<sup>+</sup> cations. The vibrational spectra and their interpretations complemented by the calculated elastic properties confirm this classification. The model-estimated piezoelectric constants allow characterizing AgTITeO<sub>3</sub> as a strong pyroelectric structure.

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#### 1. Introduction

Over the last years, the extraordinary optical properties of the  $TeO_2$ -based materials (which, from the chemical point of view, can be usually classified as tellurites) have stimulated numerous researches aimed at finding an optimal "modifiers- $TeO_2$ " composition in which such properties could be combined with quite satisfactory mechanical and thermal resistance (see [1] and references therein). Thus, it was found that the  $Tl_2O$  modifier addition allows maintaining the high optical non-linearity of the  $TeO_2$ -based materials, and, moreover, improving several other characteristics which, unfortunately, do not include good stability of the materials [2–4].

During a relevant comprehensive study of the  $(1-x)TeO_2-xTl_2O$  system, three stable  $(Tl_2TeO_3\ (x=1/2),\ \alpha-Tl_2Te_2O_5\ (x=2/3))$  and  $Tl_2Te_3O_7\ (x=3/4))$  and one metastable  $(\beta-Tl_2Te_2O_5)\ crystal-line compounds were identified <math display="inline">[2,5-8].$  (Recently, the existence of a high-temperature polymorph of  $Tl_2TeO_3$  was evidenced in [9]). The analysis of the atomic arrangements of their  $[Te_nO_{2n+1}]^{2-}$  complex tellurite-anions, jointly with the corresponding data on the other crystalline tellurites, allowed concluding that such

anions necessarily involve, at the very least, one TeO<sub>3</sub> pyramidal ortho-group which is indicative of a tellurite compound [10]. The simplest of them, having anions with n = 1 (i.e., the  $[TeO_3]^{2-}$  orthoanions), are the subjects of fundamental quantum-chemistry investigations [11], and are generally considered as the models capable of clarifying the constitutions of the ortho-tellurite glasses by performing relevant lattice-dynamical calculations [10,12,13].

All these compounds are characterized by highly asymmetric coordination of oxygen atoms around  $Te^{4+}$  and  $Tl^+$  cations (MO<sub>3</sub> trigonal pyramids and MO<sub>4</sub> disphenoids (M = Te or Tl) are classically observed [2,5–8]). This asymmetry is the direct "signature" of the presence of a stereo-active lone pair ns<sup>2</sup> and is induced by the fact that this lone pair is localized on one side of the coordination polyhedra pushing the oxygen atoms to the opposite side. On the contrary, when the lone pair is inert, the ns<sup>2</sup> electronic pair remains localized with its center on the tellurium atom and symmetric coordination environments around the cation are obtained. These cases have been observed in recent structural studies on oxide compounds containing lone pair elements (see for example, Te<sup>4+</sup> [14,15], Tl<sup>+</sup> [16] Sn<sup>2+</sup> [14], Pb<sup>2+</sup> [17], I<sup>5+</sup> [18]).

In principle, one of the possibilities to ameliorate the above mentioned shortcomings of  $TeO_2-Tl_2O$  materials is the addition of a second modifier. Consequently, a series of ternary  $TeO_2-Tl_2O-Y_kO_l$  systems are now under consideration in the SPCTS laboratory. In particular, the case Y = Ag was studied, and the data related to the relevant compounds are exposed in [19]. During that study, a new crystalline structure AgTITeO<sub>3</sub> was found. In contrast to the  $Tl_2TeO_3$  [5,6] and Ag<sub>2</sub>TeO<sub>3</sub> [20] crystalline lattices, AgTITeO<sub>3</sub> has no

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inversion center, which potentially makes the scope of its physical properties much wider, and relatively small volume of its primitive cell makes it possible to suppose that  $AgTITeO_3$  can be an intriguing object for the ab initio model investigations similar to those in Refs [11,21–23].

In the present paper, the experimental data on the structural and vibrational (Raman and infrared) properties of the  $AgTITeO_3$ lattice are communicated for the first time jointly with the latticedynamical empirical treatment including estimations of its elastic and piezoelectric constants.

#### 2. Experimental methods

AgTITeO<sub>3</sub> single crystals were synthesized by solid state reaction of equimolar amounts of Tl<sub>2</sub>TeO<sub>3</sub> and Ag<sub>2</sub>TeO<sub>3</sub> crystalline compounds. For this, Tl<sub>2</sub>TeO<sub>3</sub> was first synthesized in the laboratory by heating an intimate mixture of Tl<sub>2</sub>CO<sub>3</sub> (Aldrich, 99.9%) and TeO<sub>2</sub> (prepared in the laboratory by decomposition at 550 °C of commercial H<sub>6</sub>TeO<sub>6</sub> (Aldrich, 99.9%)) in a platinum crucible at 330 °C for 18 h, under pure flowing nitrogen and then cooling it (5 °C/min) down to room temperature. Ag<sub>2</sub>TeO<sub>3</sub> was also prepared in the laboratory by heating a mixture of Ag<sub>2</sub>O (Aldrich, 99%) and TeO<sub>2</sub> in a platinum crucible at 500 °C for 12 h under pure flowing nitrogen and then cooling it (2 °C/min) down to room temperature. The Tl<sub>2</sub>TeO<sub>3</sub>–Ag<sub>2</sub>TeO<sub>3</sub> mixture was first melted in a sealed gold tube at 600 °C for 12 h and then cooled down (0.02 °C/ min) to room temperature.

Grey, transparent AgTlTeO<sub>3</sub> single crystals suitable for X-ray diffraction study thus were obtained. The sample selected was prismatic ( $0.12 \times 0.05 \times 0.02 \text{ mm}^3$ ). Intensity data were collected with Kappa CCD (Nonius) diffractometer using monochromatized Mo K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å) under conditions reported in Table 1. A multi-scan method (SADABS [24]) was used for absorption correction.

*Infrared absorption* spectrum of the crystalline powder (dispersed in KBr or polyethylene) was recorded on a ThermoFisher 6700 spectrophotometer in the range 50 to  $1000 \text{ cm}^{-1}$ .

*Raman spectra* of the crystalline compound was recorded in the 10–1100 cm<sup>-1</sup> range and in back-scattering mode at 514.532 nm using a T64000 Jobin–Yvon spectrophotometer operating in triple substractive configuration (1800 grooves/mm) equipped with a

#### Table 1

Crystal data and structure refinement conditions for AgTeTIO<sub>3</sub>.

Tomporatura	202(2) K
	295(2) K
Formula weight	487.85 g
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Iba2
Unit cell dimensions	a = 14.708(7) Å
	b=10.745(6) Å
	c=5.166(3) Å
Volume	816.5(8) Å <sup>3</sup>
Z	8
Data collection instrument	NONIUS Kappa-CCD
Density calculated	7.937 Mg/m <sup>3</sup>
Absorption coefficient	$51.065 \mathrm{mm}^{-1}$
F (000)	1632
$\theta$ range for data collection	5.18° to 21.92°
Index ranges	-15 < h < 15, -11 < k < 11, -5 < l < 5
Reflections collected	490
Independent reflections	404 [R (int)=0.0581]
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2 (a)</sup>	1.055
Final R [I $> 2\sigma$ (I)] <sup>(b)</sup>	R1 = 0.0374, wR2 = 0.0986
R (all data)	R1 = 0.0441, wR2 = 0.1106
Extinction coefficient	0.00034(6)
Flack parameter	0.48(2)

(a) G.O.F. =  $\{\sum w(F_0^2 - F_C^2)/(N_{obs} - N_{parm})\}^{1/2}$ . (b) R1 (F) =  $\sum ||F_0| - |F_C||/|F_0|$ ;  $wR2(F^2) = \{\sum [w(F_0^2 - F_C^2)^2]/\sum [w(F_0^2)]\}^{1/2}$ . liquid nitrogen-cooled CCD detector. Measurements were made at low laser power (~2 mW on the surface of the sample), in order to avoid any damage of the crystal. The scattered light was collected through a microscope objective (x50LWD) and confocal filtering (0.1 mm). The spectral resolution was about  $2.5 \text{ cm}^{-1}$  at the exciting line.

# 3. Results and discussion

#### 3.1. Structure determination

AgTITeO<sub>3</sub> crystallizes with orthorhombic symmetry (Iba2 space group). The density measured by helium picnometry ( $\rho_{exp}$  = 7.91 ± 0.05 g.cm<sup>-3</sup>) implies Z = 8 AgTITeO<sub>3</sub> per unit cell ( $\rho_{calc}$  = 7.94 g.cm<sup>-3</sup>). The structure was solved by direct method using the SHELXS 86 program [25]. The atomic coordinates and anisotropic thermal parameters for all atoms were refined using the SHELXL-97 program [26].

The structure of AgTITeO<sub>3</sub> was refined by assuming the above mentioned non-centrosymmetric space group, undertaking and evaluating the absolute-structure. The values of the Flack parameter x [27] and its standard uncertainty u were equal to 0.48 and 0.02, respectively. From the full text of Flack and Bernardinelli [28], it was deduced that the value of u = 0.02 indicates a strong inversion-distinguishing power, and that the domains around the value of x should be well defined and clearly distinguishable from one another.

Such a parameter value indicates that the crystal is twinned by inversion. Consequently, it should be considered as constituted by a mixture of domains with inverted structures, and its absolute structure determination is not possible. A final refinement taking into account these domains by way of the TWIN/BASF instructions as recommended by SHELXL-97 program converged to final reliability factors R1 = 0.0374 and wR2 = 0.0986.

The refined atomic coordinates and thermal parameters are presented in Tables 2 and 3. Table 4 reports the main interatomic distances and angles calculated by using the Brown's method [29,30]. DIAMOND program was used for graphical representations [31].

## 3.2. Description of the structure

A projection of the unit-cell content structure onto the xOy plane and its perspective view are shown in Figs. 1 and 2, respectively. The atomic arrangements of various coordination polyhedra of cations are represented in Fig. 3. As classically observed in all thallium tellurium oxide compounds, the distribution of the chemical bonds around the Te and Tl atoms is highly anisotropic, being influenced by strong stereochemical activities of their electronic lone pairs 5 s<sup>2</sup> and 6 s<sup>2</sup>, respectively.

The three shortest Te–O bonds (1.842(10) Å, 1.859(15) Å and 1.90(2) Å, bond valence sum of 4.02) coming from each Te atom compose a distorted TeO<sub>3</sub> triangular pyramid, so that the E lone

able	2

Atomic coordinates and equivalent isotropic displacement parameters  $({\mbox{\AA}}^2)$  for AgTeTlO3.

Atom	site	Х	У	Z	U <sub>eq</sub>
Tl	8c	0.40918(6)	0.12024(5)	0.5062(3)	0.0182(6)
Ag	8c	0.25709(11)	0.12125(10)	0.0037(15)	0.0252(7)
Te	8c	0.39837(12)	0.37217(7)	0.0057(12)	0.0098(6)
O(1)	8c	0.2727(10)	0.3904(9)	0.010(7)	0.033(4)
O(2)	8c	0.4021(8)	0.2008(9)	0.010(8)	0.056(5)
O(3)	8c	0.4006(10)	0.3619(10)	0.639(4)	0.017(3)

 $U_{\rm eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor (esd are given in parentheses)

Atom	U11	U22	U33	U23	U13	U12
Tl	0.0129(7)	0.0140(7)	0.0277(7)	-0.0006(9)	-0.001(3)	0.0006(3)
Ag	0.0109(13)	0.0335(12)	0.0311(11)	-0.0008(15)	0.006(3)	-0.0098(5)
Те	0.0034(9)	0.0092(9)	0.0167(10)	0.0022(13)	-0.004(4)	-0.0009(3)
O(1)	0.017(7)	0.036(8)	0.045(8)	-0.036(13)	-0.003(18)	-0.009(5)
O(2)	0.021(7)	0.008(6)	0.140(14)	-0.039 (19)	-0.032(18)	-0.009(5)
O(3)	0.026(9)	0.018(7)	0.008(7)	-0.005(6)	-0.001(6)	-0.008(6)

**Table 3** Anisotropic displacement parameters (in  $Å^2$ ) for AgTITeO<sub>3</sub>.

The anisotropic displacement factor exponent takes the form Uij = exp  $\left[-2\pi^2(h^2a^{*2}U11 + \dots + 2hka^*b^*U22 + \dots)\right]$  (Esd's are given in parentheses)

pair of tellurium atom can be considered as a fourth vertex of a TeO<sub>3</sub>E tetrahedron (Fig. 3). Those bonds, forming O–Te–O angles of values 87.3(14), 91.9(13) and 97.8(5)° occupy one semi-sphere around the Te atom, whereas the other one is occupied by the lone pair E of the Te atom, thus representing some sort of a "dead zone" for chemical bonding. Consequently, three non-bonding Te…O contacts (2.939 Å, 3.038 Å and 3.274 Å) occurring in that zone form empty cavities (Figs. 1 and 3).

The coordination polyhedron around the atom of Tl can be described as a TlO<sub>4</sub> disphenoid in which the lone pair E of Tl is pointing in the direction of the fifth apex of a TlO<sub>4</sub>E trigonal bipyramid (Fig. 3). In this disphenoid, the four TI-O bonds have lengths ranging from 2.678(15) to 2.74(4) Å (bond valence sum of 0.93). Two of them (bonds with O(1) and O(3)) are relatively short, and two others (with O(2)) are longer. The localisation of the lone pairs E of thallium atoms in the opposite way of these four Tl-O bonds results in the formation of empty zones in the structure (Figs. 1 and 3). In contrast to Te and Tl atoms. Ag atoms (having no lone pairs) are homogeneously surrounded by six oxygen atoms forming a distorted octahedron with Ag-O distances ranging from 2.298(11) Å to 2.902(10) Å (bond valence sum of 0.94). From the packing-factor point of view; the AgTITeO<sub>3</sub> structure can be described (analogously to Tl<sub>2</sub>TeO<sub>3</sub> and Ag<sub>2</sub>TeO<sub>3</sub>) as a distorted NaCl-type structure (Fig. 1). From the crystal chemistry side, it is a typical island-type one made up from well separated fragments, namely, the molecular-like  $[TeO_3]^{2-}$  ortho-anions formed by mainly covalent Te-O bonds, and Tl<sup>+</sup> and Ag<sup>+</sup> cations electrostatically linked with the anions.

By sharing either edges or corners, TeO<sub>3</sub> pyramids, TlO<sub>4</sub> disphenoids and AgO<sub>6</sub> octahedra constitute AgTITeO<sub>3</sub> sheets parallel to the [0 1 0] direction (see Figs. 1 and 4). It is worth noting that the appearance of such sheets is due to the occurrence in the structure of the localized lone pairs of Te and Tl atoms which play the role of "structural scissors". In considering Figs. 1 and 4, one can see that: (i) the cationic ordering exists thus inducing the formation of the successive single layers of the TeO<sub>3</sub>-TlO<sub>4</sub>/AgO<sub>6</sub>/TeO<sub>3</sub>-TlO<sub>4</sub> polyhedra parallel to the [0 1 0] direction; (ii) each TlO<sub>4</sub> disphenoid is connected to three TeO<sub>3</sub> pyramids by sharing corners

Table 4

Selected bond distances (Å) and angles (°) in AgTITeO\_3 (esd are given in parentheses).

Tl-01 <sup>(i)</sup>	2.678(15)	01-Tl-03 <sup>(i)</sup>	89.6(4)
Tl-O2 <sup>(ivi)</sup>	2.71(4)	O2-TI-O2 <sup>(ivi)</sup>	88.9(7)
T1-03	2.689(12)	03-Tl-02 <sup>(ivi)</sup>	86.0(4)
T1-02	2.74(4)	01-Tl-02 <sup>(i)</sup>	88.3(8)
Ag-O2	2.298(11)	01-Ag-01 <sup>(i)</sup>	160.0(7)
Ag-O3 <sup>(ii)</sup>	2.429(16)	O3-Ag-O1 <sup>(ii)</sup>	89.9(4)
Ag-O1 <sup>(iii)</sup>	2.519(10)	O2-Ag-O3 <sup>(ii)</sup>	148.7(8)
Ag-O1 <sup>(i)</sup>	2.59(4)	O1-Ag-O1 <sup>(iii)</sup>	174.4(4)
Ag-O1 <sup>(ii)</sup>	2.65(4)	02-Ag-01 <sup>(i)</sup>	97.2(6)
Ag-O1	2.902(10)	O3-Ag-O1 <sup>(i)</sup>	86.3(10)
Te-02	1.842(10)	02-Te-01	97.8(5)
Te-01	1.859(15)	02-Te-03	87.3(14)
Te-03	1.90(2)	01-Te-03	91.9(13)

Symmetry transformation to generate equivalent atoms: i: -x + 1/2, -y + 1/2, z - 1/2; ii: -x + 1/2, -y + 1/2, z + 1/2; iii: -x + 1/2, y - 1/2, z; ivi: x, y, z - 1

or edges and to two TlO<sub>4</sub> disphenoids via O(2) corners; (iii) each AgO<sub>6</sub> octahedron is linked to four TeO<sub>3</sub> pyramids and four TlO<sub>4</sub> disphenoids via O(1) corners and to six AgO<sub>6</sub> octahedra by sharing O1–O1 edges.

## 3.3. Dynamical properties

#### 3.3.1. Lattice dynamical model

The lattice dynamical model treatment was carried out to interpret the vibrational spectra and to numerically estimate the piezoelectric and elastic properties of AgTITeO<sub>3</sub>. The LADY (LAttice DYnamics) code, which is an extended version of the CRYME (CRYstal MEchanics) program described in detail in [32], was used. The model calculations were performed by using the Valence Force



**Fig. 1.** Projection along c-axis of the AgTITeO<sub>3</sub> unit cell content (arrows visualize the stereochemically active lone pairs E of Te and Tl; the "z-positions" of Te, Tl and Ag atoms are indicated).



Fig. 2. Perspective view of the AgTITeO<sub>3</sub> unit cell content.



**Fig. 3.** The various cation coordination polyhedra. Notations for atoms are those used in Figs. 1 and 2. Arrows vizualize the direction towards which the lone pairs E are directed.

Field (VFF) approach. The IR– and Raman–intensities of the modes were estimated by using the Rigid Ion Model (RIM) and Polarizable Bond Model (PBM) approximations (see e.g. [33] and references therein), respectively. The elastic and piezo-electric constants were calculated by using the VFF and RIM parameters and theoretical formulas obtained in Refs [34,35].

During the calculations, two-body short range Te–O, Tl–O, Ag–O and O–O interactions were taken into account jointly with the



Fig. 4. Perspective view of one AgTITeO<sub>3</sub> sheet parallel to [010] direction.



Fig. 5. Experimental and calculated Raman spectra of AgTITeO<sub>3</sub>.

three-body interactions inside the O–Te–O bridges. The diagonal approximation was used to describe all the interactions, with exception for Te–O ones for which non diagonal Te–O/Te–O force constants were introduced. The Te–O bond constant, the O–O interactions, the bending force constant values and those of the non-diagonal interactions were transferred from the lattice-dynamical models, earlier elaborated for various crystalline tellurite structures [10,36,37] while the Tl–O and Ag–O force constant values were estimated as 0.07 and 0.1 mdyn/A, respectively, by fitting the calculated Raman and IR-spectra to the experimental ones. The vibrational modes were characterized by their frequencies, Raman– and IR–intensities, and atomic displacement patterns (eigenvectors given in the space of the Cartesian atomic displacements).

#### 3.3.2. Lattice vibrations

The group-theory analysis shows that the 72 brillouin zonecenter normal modes of the AgTITeO<sub>3</sub> lattice consist of the 69 vibrations distributed between irreducible representations of the  $C_{2v}$  factor group as follows:

 $\Gamma(\text{vibr}) = 17A_1 + 18A_2 + 17B_1 + 17B_2$ , to which three rigid lattice translations along z, x and y (A<sub>1</sub> + B<sub>1</sub> + B<sub>2</sub>) must be added. All the vibrations are Raman-active, whereas the A<sub>2</sub> ones are forbidden in the IR-spectrum. The measured Raman- and IR- spectra of AgTITeO<sub>3</sub> are presented in Figs. 5 and 6, respectively, jointly with the model results.



Fig. 6. Experimental and calculated infrared spectra of AgTITeO<sub>3</sub>.

d <sub>ij</sub>	ij=	15		24		31			32		33	
		8.71		-19.04		-24.11		-	-0.31		0.05	
C <sub>kl</sub>	kl=	11	22		33	2	1	31	32	44	55	66
		37.3	16.9	)	41.6	6.	3	12.1	3.7	6.1	11.1	2.8

Table 5 Calculated piezoelectric  $d_{ij}$  (10<sup>-11</sup> C/N) and elastic  $C_{kl}$  (GPa) constants for AgTITeO<sub>3</sub>.

Taking into account the island-type nature of the AgTITeO<sub>3</sub> lattice (see Section 3.2), their 69 optically-active vibrations can be specified in the terms of the internal (stretching and bending) vibrations of the TeO<sub>3</sub> anions, and their external (rotational and translational) motions to which the translational motions of Tl and Ag should be added. Consequently the vibrational spectra of AgTITeO<sub>3</sub> can be described as consisting of 12 Te–O stretchings (3A<sub>1</sub> + 3A<sub>2</sub> + 3B<sub>1</sub> + 3B<sub>2</sub>), 12 O-Te-O bendings (3 A<sub>1</sub> + 3A<sub>2</sub> + 3B<sub>1</sub> + 3B<sub>2</sub>), 12 rotational modes R (3  $A_1$  + 3 $A_2$  + 3B<sub>1</sub> + 3B<sub>2</sub>) of the TeO<sub>3</sub> units, and 33 translational modes T  $(8A_1 + 9A_2 + 8B_1 + 8B_2)$  formed by the relative displacements of those units jointly with the Tl<sup>+</sup> and Ag<sup>+</sup> cations. Taking into account that the latter 45 vibrations (12 R + 33 T) would be chiefly governed by weak oxygen-cations forces (and, moreover, include the motions of heavy bodied like TeO<sub>3</sub>, Tl and Ag), their positions should lie in the lowest-frequency domain of the spectra. This prediction is readily confirmed by the shapes of the experimental Raman and IR spectra which show that most of the vibrational bands are located below 200 cm<sup>-1</sup>, and the data deduced from the analysis of the calculated eigenvectors are in line with their above given descriptions.

From this analysis, the highest-frequency bands (600– $800 \text{ cm}^{-1}$ ) can be unambiguously attributed to the Te–O bond stretching vibrations, mainly corresponding to the motions of relatively light oxygen atoms. As to the bands lying in the interval 200–600 cm<sup>-1</sup>, their origins are not so unequivocal, being related to the O–Te–O bending forces mixed with those coming from the strongest O–O, Tl–O and Ag–O interactions. In comparing the three just indicated domains in Fig. 5 (Raman) and Fig. 6 (IR) one can see that their positions in the Raman scattering and IR-absorption do not differ markedly, thus indicating the weakness of the factor-group splitting.

According to the calculations, the external vibrations of TeO<sub>3</sub>, as well as the Tl and Ag cation motions are mainly governed by weak forces corresponding to interatomic separation longer than 2.3 Å originating from the anion-anion and anion-cation interactions. The cation motions are essentially mixed with  $[TeO_3]^{2-}$  complex anion translations and rotations. Since, on the one hand, the shortest Ag-O interactions (2.3 Å), are stronger than the Tl-O ones (2.6 Å), and on the other hand, the Ag atoms are markedly lighter than the atoms of Tl and the TeO<sub>3</sub> units are, the modes lying between 170–220 cm<sup>-1</sup> were found to be mainly related to the motions of Ag, whereas the lowest part of the spectrum is dominated by Tl-O bond, and by weak interactions between TeO<sub>3</sub> pyramids. The existence of exceptionally low-frequency bands  $(down to 20 cm^{-1})$  predicted by our model calculations both for Raman and IR spectra seems to be quite adequate to physical reality as it can be seen in Fig. 5, and can be correlated to a typical feature of the ortho-tellurite vibrational spectra due to a great mass of the TeO<sub>3</sub>. (The recent ab initio calculations of the vibrational spectra of the Li<sub>2</sub>TeO<sub>3</sub> lattice [11] revealed several modes lying near  $30 \text{ cm}^{-1}$ ).

If (as it is traditionally done) the  $[TeO_3]^{2-}$  anion is considered in  $C_{3V}$  symmetry approximation, its stretching and bending vibrations could be described as the  $A_1 + E$  ones of a AX<sub>3</sub> pyramid-like

molecule [38]. However, according to our model calculations, the high splitting and intensities of the band lying near 719 and 635 cm<sup>-1</sup> in the Raman spectrum of AgTITeO<sub>3</sub> originate from the strong asymmetry of TeO<sub>3</sub> pyramids (according to Table 5, the Te– O bond lengths are very different). Consequently, the language of the trivial symmetry seems to be much more convenient for this TeO<sub>3</sub> pyramids structure than that of C<sub>3v</sub> group.

Generally, the Raman and IR– spectra of the AgTITeO<sub>3</sub> lattice are in full correspondence with its crystal chemistry characteristics given in Section 3.2. Those spectra, in fact, reflect the properties intrinsic in "genuine" ortho-tellurite structures (like e.g.,  $Tl_2TeO_3$ and Ag<sub>2</sub>TeO<sub>3</sub>) to which the AgTITeO<sub>3</sub> structure should be apparently attributed.

## 3.3.3. Elasticity and piezoelectricity

Belonging to the  $C_{2v}$  crystallographic class, the AgTITeO<sub>3</sub> lattice would have a permanent (but temperature-dependent) macroscopic polarization defined by a vector P oriented along the Z axis. The crystal polarisation variations induced by homogeneous stresses (in the Voigt notations [39]) specify its tensor of piezoelectric modules  $d_{ij}$ . The non-zero elastic and piezoelectric matrix elements for AgTITeO<sub>3</sub> are presented in Table 5.

It can be mentioned that the piezoelectric constant values thus obtained are close to the relevant characteristics found for the best oxide piezoelectrics, which can be also regarded as a marker of a high pyroelectricity of AgTITeO<sub>3</sub>. We venture the opinion that, if so, strong second-harmonic generation effects can then be expected for it.

The model-estimated values of the  $C_{kl}$  elastic constants given in Table 5 seem to be quite reasonable, with exception for the shear constant values which can be suspected as to be underestimated because of the exclusively two-body character of the forces considered in coordination polyhedra around Ag and Tl atoms.

## 4. Conclusion

The structural and vibrational properties of a new AgTITeO<sub>3</sub> crystal were determined, allowing us to classify it as a typical island-type compound whose anionic part is formed from the practically isolated  $[TeO_3]^{2-}$  ortho- anions, whereas the cationic part is made from the Ag<sup>+</sup> and Tl<sup>+</sup> ions. The model-estimated elastic constants show a strong anisotropy of the shear elasticity thus in agreement with the layer-like crystal chemistry constitution of this structure, whereas the values of calculated piezoelectric tensor elements specify it as a strong pyro-electric in which, theoretically, second-order non-linear optical effects can be generated.

#### References

- R.A.F. El-Mallawany, Tellurite Glasses Handbook: Properties and data, CRC Press, Boka Raton, FL, 2002.
- [2] B. Jeansannetas, P. Marchet, P. Thomas, J.C. Champarnaud-Mesjard, B. Frit, J. Mater. Chem. 8 (4) (1998) 1039–1042.

- [3] B. Jeansannetas, S. Blanchandin, P. Thomas, P. Marchet, J.C. Champarnaud-Mesjard, T. Merle-Méjean, B. Frit, V. Nazabal, E. Fargin, G. Le Flem, M.O. Martin, B. Bousquet, L. Canioni, S. Le Boiteux, P. Segonds, L. Sarger, J. Solid State Chem. 146 (1999) 329–335.
- [4] M. Dutreilh-Colas, P. Thomas, J.C. Champarnaud-Mesjard, E. Fargin, J. Phys. Chem. Glasses 44 (5) (2003) 349–352.
- [5] B. Frit, D. Mercurio, Rev. Chim. Min. 17 (1980) 192-201.
- [6] B. Frit, D. Mercurio, P. Thomas, J.C. Champarnaud-Mesjard, Z. Kristallogr, NCS 214 (1999) 439–440.
- [7] B. Jeansannetas, P. Thomas, J.C. Champarnaud-Mesjard, B. Frit, Mater. Res. Bull. 32 (1) (1997) 51–58.
- [8] B. Jeansannetas, P. Thomas, J.C. Champarnaud-Mesjard, B. Frit, Mater. Res. Bull. 33 (11) (1998) 1709–1716.
- [9] F. Rieger, A.V. Mudring, Inorg. Chem. 46 (2007) 446-452.
- [10] A.P. Mirgorodsky, T. Merle-Méjean, P. Thomas, J.C. Champarnaud-Mesjard, B. Frit, J. Phys. Chem. Solids 63 (2002) 545–554.
- [11] L. D'Alessio, F. Pietrucci, M. Bernasconi, J. Phys. Chem. Solids 68 (2007) 438-444.
- [12] O. Noguera, T. Merle-Méjean, A.P. Mirgorodsky, P. Thomas, J.C. Champarnaud-Mesjard, J. Phys. Chem. Solids 65 (2004) 981–993.
- [13] M. Soulis, A.P. Mirgorodsky, T. Merle-Méjean, O. Masson, P. Thomas, M. Udovic, J. Non-Cryst. Solids 354 (2008) 143-149.
- [14] Z. Mayerova, M. Johnsson, S. Lidin, Angew. Chem. Int. Ed. 45 (2006) 5602–5606.
  [15] P.S. Halasyamani, Chem. Mater. 16 (2004) 3586–3592.
- [16] A. Grzechnik, P.S. Halasyamani, H. Young Chang, K. Friese, J. Solid State Chem. 182 (2009) 1570–1574.
- [17] M. Lin Hu, Y. Ping Lu, H. Min Zhang, B. Tu, Z. Min Jin, Inorg. Chem. Commun. 9 (2006) 962–965.
- [18] J. Yeon, S.-H. Kim, P.S. Halasyamani, J. Solid State Chem. 182 (2009) 3269– 3274.
- [19] d. linda, M. Dutreilh-Colas, P. Thomas, A.P. Mirgorodsky, J.R. Duclere, O. Masson, M. Loukil, A. Kabadou, Mater. Res. Bul., (under review).
- [20] R. Masse, J.C. Guitel, I. Tordjman, Mater. Res. Bull. 15 (1980) 431-436.

- [21] M. Ceriotti, F. Pietrucci, M. Bernasconi, Phys. Rev. B. 73 (2006), 104304-1-1104304-17.
- [22] M. Ben Yahia, E. Orhan, A. Beltran, O. Masson, T. Merle-Méjean, A.P. Mirgorodsky, P. Thomas, J. Phys. Chem. B 112 (2008) 10777–10781.
- [23] N. Berkaine, Ph.D. thesis, University of Limoges (2009), http://www.unilim.fr/scd/
- [24] SADABS, Brüker AXS Inc., Madison, Wisconsin, USA (2001).
- [25] G. M. Sheldrick, Shelxs-86, program for the solution of Crystal structures, University of Göttingen, Germany, (1997).
- [26] G. M.Sheldrick, ShelxL-97, program for Crystal structure determination, University of Göttingen, Germany, (1997).
- [27] H.D. Flack, Acta Cryst. A39 (1983) 876-881.
- [28] H.D. Flack, G. Bernardinelli, J. Appl. Cryst. 33 (2000) 1143-1148.
- [29] I.D. Brown, D. Atermatt, Acta Cryst. B41 (1985) 244-247.
- [30] N.E. Brese, M.O. Keeffe, Acta Cryst. B47 (1991) 192-197.
- [31] K. Brandenburg, DIAMOND, Crystal Impact GbR, Version 2.1e, Bonn, Germany, (2001).
- [32] M.B. Smirnov, A.P. Mirgorodsky, P.E. Quintard, J. Mol. Structure 348 (1995) 159– 162.
- [33] J. Cornette, T. Merle-Méjean, A. P. Mirgorodsky, M. Colas, M. Smirnov, O. Masson, P. Thomas, J. Raman Spectroscopy, (in press) (2010).
- [34] A.N. Lazarev, A.P. Mirgorodsky, J. Phys. Chem. Minerals 18 (1991) 231-243.
- [35] A.P. Mirgorodsky, M.B. Smirnov, E. Abdelmoumîn, T. Merle-Méjean, P.E. Quintard, Phys. Rev. B 52 (1994) 3993–4000.
- [36] A.P. Mirgorodsky, T. Merle-Méjean, J.C. Champarnaud-Mesjard, P. Thomas, B. Frit, J. Phys. Chem. Solids 61 (2000) 501–509.
- [37] J.C. Champarnaud-Mesjard, S. Blanchandin, P. Thomas, A.P. Mirgorodsky, T. Merle-Méjean, B. Frit, J. Phys. Chem. Solids 61 (2000) 1499–1507.
- [38] K. Nakamato, Infrared Spectra of inorganic, Coordination Compounds, Wiley, New York-Singapore, 1986.
- [39] M. Born, H. Kun, Dynamical Theory of crystal lattices (1988), Clarendon PRESS OXFORD.