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A New Lithium Hydrogen Tellurate—LiH_5TeO_6

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X-ray structural analysis for lithium pentahydrogen tellurate has been carried out. The substance crystallizes in a tetragonal system in the space group $P4_2/n$, $a = 7.6350(6)$, $c = 7.5014(9)$ Å, $V = 437.28(7)$ Å^3, $Z = 4$, and $R = 0.0189$ for 350 observed reflections. The crystal structure consists of isolated TeO_6 octahedra, which are connected by a network of hydrogen bonds. The lithium atoms are surrounded by slightly deformed oxygen octahedra. Infrared and Raman spectra have been studied. The FTIR spectra were recorded down to a temperature of 90 K. Thermal behavior of LiH_5TeO_6 has been studied by the methods of TG, DTA, DTG, and DSC. Conclusions following from the DSC and FTIR measurements exclude the existence of structural phase transitions in the temperature interval from 90 K to the temperature of decomposition of the compound (390 K).

INTRODUCTION

A great deal of attention was paid to the study of the tellurates and hydrogen tellurates of the alkali metals, as these substances are especially interesting from a structural standpoint. So far, the crystal structures of the following lithium tellurates have been solved: $Li_8Te_2O_{10}$ (1), Li_2TeO_4 (2), and Li_6TeO_6 (3, 4).

In contrast to sodium and potassium hydrogen tellurates, however, no structure has been elucidated for lithium hydrogen tellurate. This reflects the difficulty of preparing crystals of these compounds suitable for structural analysis.

On the basis of knowledge of the structural arrangement, a number of the hydrogen tellurates of alkali metals can be considered potential ionic (proton) conductors, which fulfill the basic theoretical conditions for the existence of such properties (5). These conclusions are also supported by the fact that fast proton conductivity was observed and studied for the related compounds of sulfur and selenium (6, 7).

The present work, which belongs to the framework of our systematic study of selected hydrogen-bonded solids, deals with preparation, crystal structure determination, study of vibrational spectra, and thermal behavior of the first known lithium hydrogen tellurate—LiH_5TeO_6.

EXPERIMENTAL

The substance was prepared by addition of an equivalent amount of crystalline hexahydrogen telluric acid (Aldrich) to LiOH solution (2 mol dm^{-3}, Lachema). Following 2 h of intense stirring, the reaction mixture was filtered through filter paper and the filtrate was left to crystallize in a closed crystallization vessel at 298 K. The crystals separated after 6 months were washed with distilled water and ethanol and dried at laboratory temperature in the air. The colorless crystals obtained are insoluble in water and, similar to most of the alkali metals hydrogen tellurates, are readily soluble in concentrated hydrochloric acid.

The determination of tellurium was carried out both gravimetrically (8) (theoretical content, 54.17%; found, 54.12%) and by the AAS method (found 54.09%) using the flame technique (air–acetylene). The measurement was carried out on the Varian Techtron Model 1200 instrument. Elemental analysis of the alkali metal was carried out by the AAS method under the same conditions as for Te (theoretical content, 2.95%; found, 2.86%). Thermogravimetry (TG) was performed using a Derivatograph OD 102 instrument (MOM Budapest). The experiments were carried out in an atmosphere of static air, using sample masses of approximately 250–300 mg in platinium sample pans and heating at 10 K/min from an ambient temperature to a maximum temperature of 873 K. TG, DTA, and DTG recordings were made.

The DSC measurements were carried out on a Perkin–Elmer DSC 7 power-compensated apparatus in the 95–373 K temperature range (helium atmosphere). A heating rate of 10 K/min was selected to measure approximately 10 mg of finely ground sample placed in an aluminum capsule.

Infrared spectra of nujol mulls were recorded on a Mattson Genesis FTIR spectrometer in the 400–4000 cm^{-1}

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region (resolution, 2 cm^{-1}; Beer–Norton medium apodization). Low-temperature measurements were carried out by the nujol mull method in low-temperature cell with KBr windows down to 90 K. The temperature was controlled by an Fe-Const. thermocouple. The analog signal was processed on a PC using the AX5232 temperature measurement board. The Raman spectra were recorded on a Bruker Equinox 55/S FTIR spectrometer with FRA 106/S Raman module (2 cm^{-1} resolution, Blackman–Harris 4-term apodization, 1064 nm NdYAG laser excitation, 300 mW power at the sample) in the 50–3600 cm^{-1} region.

The X-ray data collection for the LiH_5TeO_6 single crystal was carried out on an Enraf–Nonius CAD4-MACH III four-circle diffractometer (Mo$K\alpha$, graphite monochromator). Intensities of diffractions were corrected for Lorentz-polarization effects and for absorption using a numerical method (9).

The crystals suffered merohedric twinning from the Laue group $4/m$ to $4/mmm$; however, the positions of telluric atoms are invariant under the twinning operation and enabled the easy solution of the phase problem by heavy atom methods (10). The twinning was included in the following calculations using the transformation matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

for *hkl* indices and ratio of two individuals were refined to 0.450(5). The nonhydrogen atoms were refined anisotropically using the full-matrix least-squares procedure. The positions of hydrogen atoms were found from the difference map and fixed in position with temperature factor $U_{\mathrm{iso}} = 0.06$ Å^2, because of instability of the refinement. One hydrogen atom (H2) is disordered into two positions generated by a twofold axis in accordance with the number of hydrogen atoms in the formula.

The basic crystallographic data and the details of the measurement and refinement are summarized in Table 1. A list of the observed and calculated structural factors and the anisotropic displacement factors is available from the authors upon request.

RESULTS AND DISCUSSION

The Crystal Structure of LiH_5TeO_6

The atomic coordinates are given in Table 2, and the bond lengths and angles, including those for the hydrogen bonds, are listed in Table 3. The atom numbering and the packing scheme can be seen in Fig. 1.

The unit cell of LiH_5TeO_6, similar to known modifications of hexahydrogen telluric acid (11–13), consists of isolated TeO_6 octahedra connected by a network of hydrogen bonds.

TABLE 1
Basic Crystallographic Data, Data Collection, and Refinement Parameters

Empirical formula	LiH_5TeO_6
Formula weight	235.58
Crystal system	Tetragonal
Space group	$P4_2/n$
Unit cell dimensions	$a = 7.6350$ (6) Å $c = 7.5014$ (9) Å $V = 437.28$ (7) Å^3
Z	4
Calculated density	$D_c = 3.578$ Mg m^{-3}
Absorption coefficient	$\mu = 6.733$ mm^{-1}
F (000)	432
Diffractometer and radiation used	Enraf–Nonius CAD4-MACH III, Mo$K\alpha$, $\lambda = 0.71069$ Å
Scan technique	ω–2θ
Number and θ range of reflections for lattice parameter refinement	25, 14–16°
Range of h, k, and l	$-9 \rightarrow 9$, $-9 \rightarrow 9$, $0 \rightarrow 8$
Number of standard reflections	3
Standard reflection monitored in interval	60 min
Intensity variation	1.3%
Total number of reflections measured	1523
θ range	2.67–24.97°
Number of independent reflections (R_{int})	387 (0.023)
Number of observed reflections	350
Criterion for observed reflections	$I > 2\sigma(I)$
Absorption correction	Numerical
T_{min}	0.509
T_{max}	0.574
Function minimized	F^2
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0239P)^2 + 0.32P]$ $P = (F_0^2 + 2F_c^2)/3$
Reflections collected/unique	1523/386
Data/restraints/parameters refined	386/0/42
Goodness-of-fit on F^2	1.233
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0189$, w$R2 = 0.0517$
R indices (all data)	$R1 = 0.0218$, w$R2 = 0.0536$
Extinction coefficient	0.0088 (10)
Maximum and minimum heights in final $\Delta\rho$ map	1.04, -0.34 e.Å^{-3}
Source of atomic scattering factors	International Tables for X-Ray Crystallography Vol. C, Table 4.2.6.8
Programs used	SHELXL 97, JANA 98

It follows from the values of the angles (see Table 3) that TeO_6 octahedra are subject to only minimum distortion. The degree of distortion, which is affected by the number and positions of the lithium cations and properties of the hydrogen bonds present, is somewhat greater than in the cubic H_6TeO_6 (13).

The length of the Te–O bond varies between 1.91 and 1.93 Å, i.e., in the range of lengths that occur most frequently

TABLE 2

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent (for Non-H Atoms $\times 10^3$) or Isotropic (for H Atoms $\times 10^3$) Displacement Factors with Standard Deviations in Brackets $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

	x	y	z	U_{eq}(Å^2)
Te	0	0	0	13 (1)
Li	0	0	5000	27 (3)
O(1)	− 2317(3)	− 503(3)	− 877(3)	22 (1)
O(2)	− 719(3)	2312(4)	666(3)	21 (1)
O(3)	678(4)	790(3)	− 2320(3)	16 (1)
H(1)	− 2395	25	− 2241	60
H(2)	− 2200	2350	620	60
H(3)	594	2012	− 2326	60

for compounds of Te(VI), where this bond length occurs in about 57% of cases (14). Similarly for both modifications of H_6TeO_6, the length of these bonds has a value of about 1.91 Å.

Every lithium cation is surrounded in the structure by six oxygen atoms, which form a slightly deformed octahedron around it (Li–O distances in the range 2.16 to 2.19 Å). This octahedron is characterized by a greater degree of deformation than the octahedra around the Te atom.

TABLE 3

Bond Lengths (Å) and Selected Angles (°)

Te–O(1)	1.926 (3)	O(2)–Te–O(1)	90.56 (9)
Te–O(2)	1.915 (3)	O(3)–Te–O(2)	91.39 (11)
Te–O(3)	1.913 (19)	O(2)^{i}–Te–O(1)	89.44 (9)
Li–O(1)^{v}	2.185 (2)	O(3)–Te–O(1)	90.05 (10)
Li–O(2)^{iii}	2.182 (3)	O(3)^{i}–Te–O(1)	89.95 (10)
Li–O(3)^{i}	2.162 (19)	O(3)^{i}–Te–O(2)	88.61 (11)
		O(2)^{iii}–Li–O(1)^{v}	89.92 (8)
		O(3)^{ii}–Li–O(2)^{iii}	86.69 (11)
		O(3)^{i}–Li–O(2)^{iii}	93.31 (11)
		O(3)^{i}–Li–O(2)^{iv}	89.69 (11)
		O(3)^{i}–Li–O(1)^{v}	91.36 (9)
		O(3)^{ii}–Li–O(1)^{v}	88.64 (9)
		Te–O(1)–H(1)	107.1 (2)
		Te–O(2)–H(2)	107.6 (2)
		Te–O(3)–H(3)	107.5 (2)

Hydrogen bonds

Donor–H	Donor…Acceptor	H…Acceptor	Donor–H…Acceptor
O(1)–H(1)	O(1)…O(2)^{iii}	H(1)…O(2)^{iii}	O(1)–H(1)…O(2)^{iii}
1.102(2)	2.770(4)	1.672(3)	174.6(2)
O(2)–H(2)	O(2)…O(2)^{vi}	H(2)…O(2)^{vi}	O(2)–H(2)…O(2)^{vi}
1.132(2)	2.735(5)	1.610(2)	171.7(1)
O(3)–H(3)	O(3)…O(3)^{vii}	H(3)…O(3)^{vii}	O(3)–H(3)…O(3)^{vii}
0.935(3)	2.711(3)	1.790(3)	168.0(1)

Note. Equivalent positions: (i) $x, y, z-1$; (ii) $-y, x+1/2, z-1/2$; (iii) $y-1/2, -x, z-1/2$; (iv) $-x, -y, -z$; (v) $-y, x+1/2, z+1/2$; (vi) $-x-1/2, -y+1/2, z$; (vii) $y, -x+1/2, -z-1/2$.

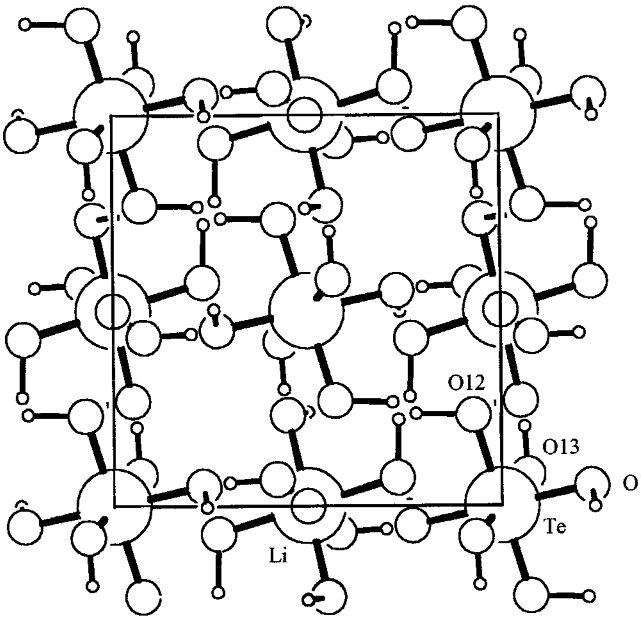

FIG. 1. Packing scheme of LiH_5TeO_6 (projection to xy plane). Hydrogen bonds are not projected.

The lengths of the O–H…O hydrogen bonds vary in the range 2.71 to 2.77 Å (see Table 3). These bonds are comparable to H bonds found in monoclinic H_6TeO_6, which attain values in the interval from 2.70 to 2.73 Å (11). In contrast, for the cubic modification of telluric acid, two types (according to length) of H bonds are present in crystal structure i.e., bonds with a length of 2.64 and 2.77 Å (13).

A joint characteristic of LiH_5TeO_6 and both modifications of H_6TeO_6 is undoubtedly the existence of isolated TeO_6 octahedra connected by a system of hydrogen bonds and thus forming a three-dimensional structural network.

Analysis of the Vibrational Spectra

The number of normal modes of the LiH_5TeO_6 crystal was determined by nuclear site group analysis (15). The crystals belong in the $P4_2/n$ (C_{4h}^4) space group with eight atoms per asymmetric unit ($Z = 4$). The atoms of Te and Li occupy fourfold positions $c(C_i)$ and $d(C_i)$, respectively. The atoms of O and H occupy eightfold positions $g(C_1)$. Two types of species present in the unit cell, $H_5TeO_6^-$ and Li^+, occupying fourfold positions $c(C_i)$ and $d(C_i)$, respectively, were considered in more detailed calculations of the internal and external modes. The results are the representations $3A_g(\mathrm{RA}) + 6A_u(\mathrm{IR}) + 3B_g(\mathrm{RA}) + 6B_u + 3E_g(\mathrm{RA}) + 6E_u(\mathrm{IR})$ for external modes and $15A_g(\mathrm{RA}) + 18A_u(\mathrm{IR}) + 15B_g(\mathrm{RA}) + 18B_u + 15E_g(\mathrm{RA}) + 18E_u(\mathrm{IR})$ for internal modes.

Standard correlation methods (16) were used for more detailed study of the expected vibrational features of

TABLE 4
Correlation Analysis of TeO_6 Internal Modes in LiH_5TeO_6 Crystal

Free ion modes	Degree of freedom	Free ion symmetry O_h	Site symmetry C_i	Factor group symmetry C_{4h}	Vibration modes	Activity	
						IR	Raman
ν_1	4	A_{1g}		A_g	$\nu_1, 2\nu_2, 3\nu_5$		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
ν_2	4	E_g	A_g	A_u	$3\nu_3, 3\nu_4, 3\nu_6$	z	
ν_3	4	F_{1u}		B_g	$\nu_1, 2\nu_2, 3\nu_5$		$\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$
ν_4	4	F_{1u}	A_u	B_u	$3\nu_3, 3\nu_4, 3\nu_6$		
ν_5	4	F_{2g}		E_g	$\nu_1, 2\nu_2, 3\nu_5$		α_{xz}, α_{yz}
ν_6	4	F_{2u}		E_u	$3\nu_3, 3\nu_4, 3\nu_6$	x, y	

the tellurate group. The results obtained are presented in Table 4.

In contrast to expectations of a marked difference in the infrared and Raman spectra following from the conclusions of the correlation analysis (see Table 4), it is apparent from the results obtained (see Fig. 2) that, in the region from 400 cm^{-1}, the spectra basically differ only in the intensity of the bands of the δ Te–O–H and ν O–H…O vibrations. Even the expected stronger correlation field splitting was not observed in the spectra.

Vibrational Spectra of LiH_5TeO_6

The IR spectra of LiH_5TeO_6 recorded at laboratory and low temperatures (90 K) are depicted in Fig. 2 together with the Raman spectrum; the peak positions are listed in

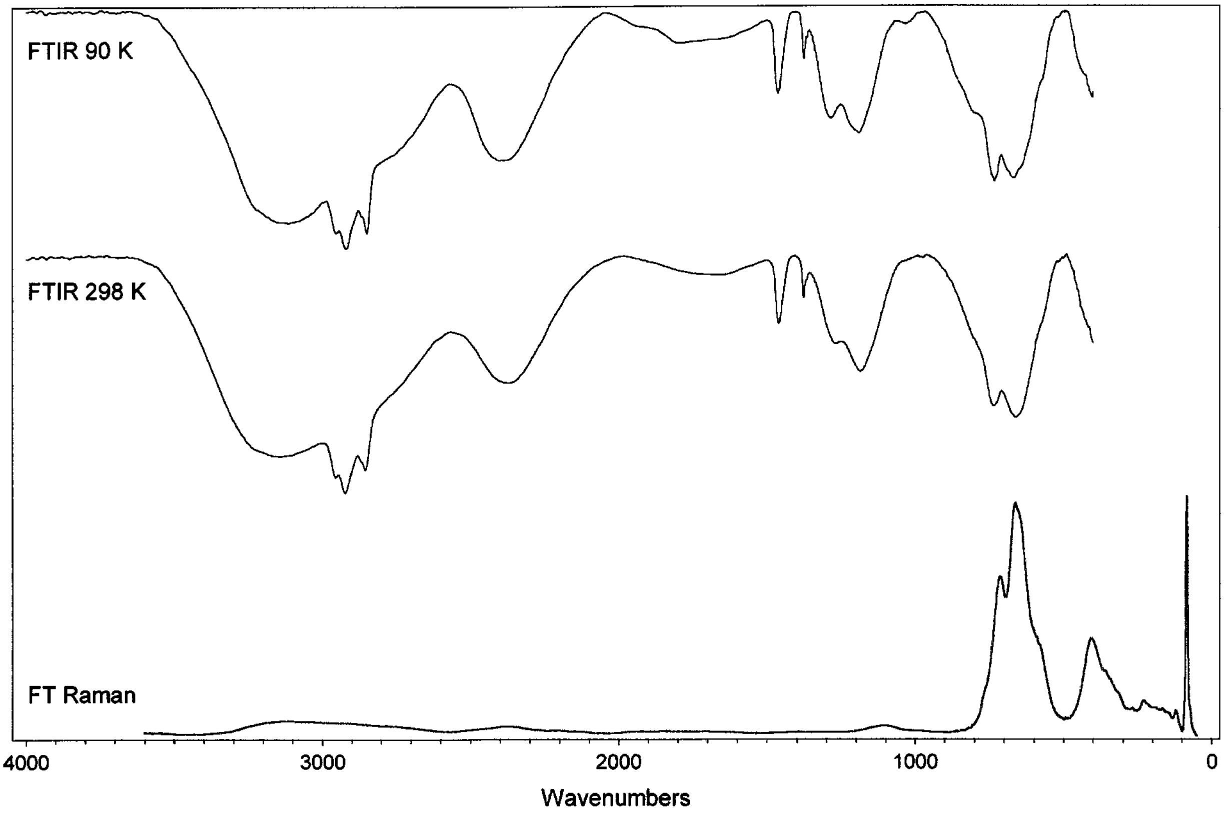

FIG. 2. FTIR (nujol mull) and FT Raman spectra of LiH_5TeO_6.

TABLE 5
FTIR and FT Raman Spectra of LiH_5TeO_6 (cm^{-1})

	IR		Raman
Assignment	298 K	90 K	(peak intensity)
νO–H…O	3140sb	3120sb	3100(6)
	2375mb[a]	2390mb[a]	2370(4)[a]
?		1925sh	
		1800wb	
	1675wb	1645sh	
δTe–O–H	1269m	1284m	
	1180m	1189m	1100(4)
?		1030wb	
νTe–O, γO–H…O	800sh	800sh	
νTe–O	734s	733s	713(67)
	661s	668s	663(98)
		575sh	585sh
δO–Te–O	400m	403m	407(41)
			230(15)
External modes			167(12)
			147(10)
			121(11)
			85(100)

[a] Fermi resonance with 2δTe–O–H.

Note. Abbreviations used: s, strong; m, medium; w, weak; b, broad; sh, shoulder; ν, stretching; δ, deformation or in-plane bending; γ, out-of-plane bending.

Table 5. The dominant bands from the standpoint of intensity in the infrared spectra are the stretching vibrations of the OH groups participating in the system of hydrogen bonds. Their position (center of the band at about 3100 cm^{-1}) fully corresponds (17) to manifestations of the hydrogen bonds found with lengths of 2.71 to 2.77 Å. During cooling of the sample to a temperature of 90 K, there is a shift in this band by 20 cm^{-1} to lower wavenumbers. A further characteristic band for these acidic salts is the medium intensity band of the δ Te–O–H deformation vibration at 1200 cm^{-1}. The band is clearly split into a doublet that remains unchanged even at decreased temperature and is shifted by 10–15 cm^{-1} to higher wavenumbers. Similar thermal behavior is also exhibited by the medium broad band at 2375 cm^{-1}. In agreement with the literature (18), this band could be assigned on the basis of its position to the overtone 2δ Te–O–H; however, the fact that the intensity of the discussed band is much higher than for the fundamental vibration, together with the absence of the original splitting into a doublet, leads to the conclusion that, similar to acid selenites (19), this band is a product of the Fermi resonance of the ν O–H…O stretching modes with the overtones of the bending vibrations 2δ Te–O–H. The result of the Fermi resonance is thus the characteristic AB band in the 3500–2000 cm^{-1} region. The out-of-plane bending modes of the hydrogen bonds are apparently manifested in the shoulder at 800 cm^{-1}, which is more clearly separated at lower temperatures.

The bands of the valence vibrations of Te–O are located in the spectra in the 800–500 cm^{-1} region. It is surprising that their position and intensity are practically identical in the IR and Raman spectra. Thus, in the absence of the polarization measurement of the LiH_5TeO_6 single crystal, it is not possible to interpret the observed bands in detail.

The medium intensity bands at 400 cm^{-1} (IR, Raman) and 230 cm^{-1} (Raman) are characteristic for the O–Te–O deformation vibrations. The low number of these bands, and also of the bands of the Te–O stretching vibrations, in agreement with the results of the X-ray structure determination of this substance, indicates that the structure of LiH_5TeO_6 consists of only monomers derived from the H_6TeO_6 octahedra, without any polycondensation of these species.

In the Raman spectra in the region below 200 cm^{-1}, in addition to the external modes, it is also possible to expect manifestations of ν (OH)⋯O vibrations of the hydrogen bonds (20).

Thermal Behavior

The recording of the TG, DTG, and DTA curves of LiH_5TeO_6 is depicted in Fig. 3. Gradual thermal decomposition, which can be depicted schematically as

$$LiH_5TeO_6 \rightarrow LiHTeO_4 + 2H_2O,$$

occurs in a single step in the temperature range 393–483 K (calculated loss in the weight of H_2O, 15.3%; experimentally found, 15.3%). Similar thermal behavior was also observed (21) for the analogous hydrogen tellurates of the MH_5TeO_6 type (M = Na, K).

Compounds were further studied by the DSC method from a temperature of 95 K up to a temperature immediately prior to the beginning of the decomposition process (390 K). No thermal effect was observed in the entire temperature interval.

The FTIR spectra were recorded in the temperature interval from 298 to 90 K. No changes that would indicate the occurrence of structural phase transition were observed during the decrease in the temperature of the sample.

The conclusions following from the DSC and FTIR measurements exclude the possibility of the existence of phase transitions for LiH_5TeO_6 from 90 K up to a temperature immediately prior to the beginning of the decomposition process. The fact that the test compound does not undergo phase transitions that are characteristic for structurally similar proton conductors leads to the conclusion that ion (proton) conductivity of lithium pentahydrogen tellurate is improbable. Because of the centrosymmetric

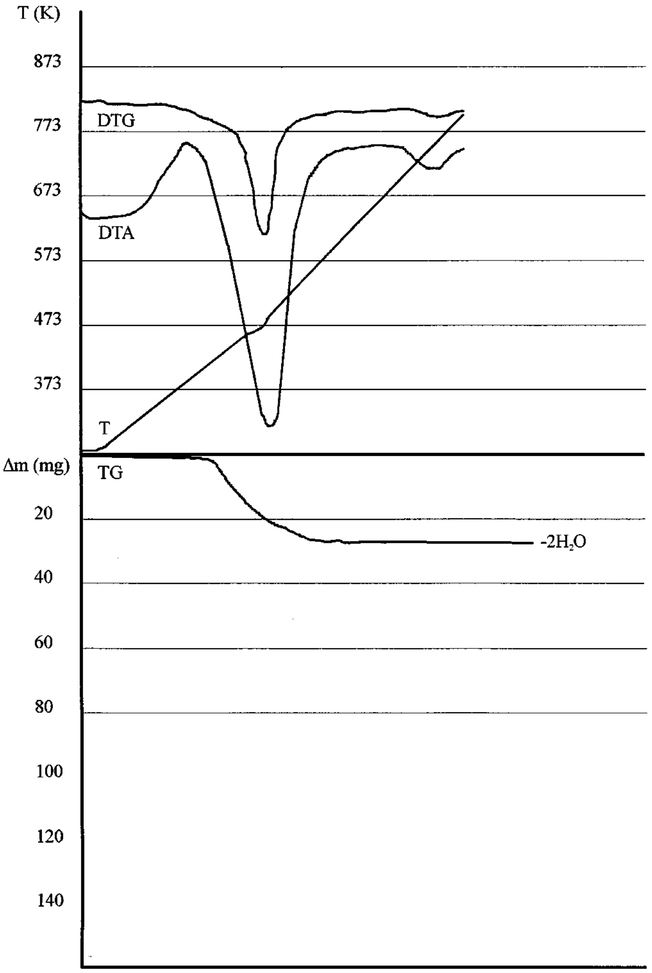

FIG. 3. Recording of the thermal decomposition of LiH_5TeO_6.

nature of the crystal space groups, it is apparent that LiH_5TeO_6 also can not exhibit the physical properties connected with the existence of spontaneous polarization.

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