Structural, dielectric and thermal properties of TlH$_2$AsO$_4$

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Abstract. Structural (at room temperature) and dielectric and thermal properties of
TlH$_2$AsO$_4$ have been studied as functions of temperature to understand the existence of
its reported phase transition. The space group and cell parameters of the compound were
determined. The crystal structure was determined by Patterson and Fourier difference
methods and refined by the full-matrix least-squares technique. The structure can be
explained in terms of zig-zag chains of H-bonds running along the c-axis. Careful studies
on dielectric and thermal properties of the substance do not suggest any ferroelectric
phase transitions in it.

Keywords. Crystal structure; phase transitions; hydrogen-bonding; chain type structure;
dielectric and thermal properties.

1. Introduction

Thallium (I) dihydrogen arsenate, TlH$_2$AsO$_4$ (TDA) and thallium dihydrogen
phosphate, TlH$_2$PO$_4$ (TDP) are considered as members of KH$_2$PO$_4$-type (KDP)
compounds. Although enormous amount of work has been done on KDP-type of
H-bonded ferro and antiferroelectric crystals, not much is known about TDA and
their deuterated compounds except a few studies on TDP such as neutron diffrac-
tion (Choudhary and Nelmes 1978a; Nelmes and Choudhary 1981), X-ray diffrac-
tion (Oddon et al 1979), calorimetric and dielectric measurements (Matsuo and
Suga 1977; Narasaiah and Choudhary 1987), Raman spectroscopic analysis (Huong
et al 1975; Narasaiah et al 1987) and pressure dependence of the dielectric constant
(Yasuda et al 1979). TDP and its deuterated compounds, TlD$_2$PO$_4$ (DTDP) have
been shown to have phase transitions at 230 and 350 K respectively (Yasuda et al
1979). They were concluded as antiferroelectrics based on their dielectric and
polarisation properties. Structural but ferroelectric phase transition in TDA was
reported (Milia 1977; Blinc et al 1978) on the basis of their proton spin lattice relax-
ation study.

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As the crystal structure of TDA is not known to be isomorphous with TDP (Nelmes and Choudhary 1981), it is interesting to study the structural, dielectric and thermal properties of this compound for better understanding of the existence of ferroelectrics phase transition.

2. Experimental

The TlH_2AsO_4 compound was prepared from a stoichemetric mixture of thallium carbonate, Tl_2CO_3 (Johnson Mattey Chemicals Ltd. 99·9% pure), and ortho-arsenic acid (99%, BDH chemicals) at room temperature (300 K). Colourless thin needle-shaped single crystals of TDA were obtained by slow evaporation of super-saturated solution of the compound.

For structural analysis, a crystal of approximate size $0·5 \times 0·4 \times 0·07\, mm^3$ was used. Accurate cell parameters were obtained by least-squares refinement of 25 carefully centred high-angle reflections. The crystal data are: formula: TlH_2AsO_4, $M_r = 345·3°$, monoclinic, $a = 6·015(1)\,Å$, $b = 4·635(2)\,Å$, $c = 14·52(2)\,Å$, $\beta = 92·48(1)°$, $V = 445·14(3)\,Å$. Systematic absences were $h0l$ with l odd; $0k0$ with k odd. The space group was identified as $P2_1/c$ with four formula units in the cell. The calculated density and μ were found to be $5·10(2)\, gm\, cm^{-3}$ and $822·56\, cm^{-1}$ respectively. The intensity measurements were made on an Enraf–Nonius CAD-4) automatic diffractometer using graphite monochromatized $MoK\alpha$ radiation. The θ-2θ scanning mode was used for collecting data in the range $4 \leqslant 2\theta \leqslant 50°$, hence $(\sin\theta/\lambda)_{max} = 0·51\,Å^{-1}$. Two standard reflections were measured for every sixty reflections, and no significant variation was found [i.e. not more than $2\sigma(I)$] in their intensities with time. A total of 2968 reflections (including systematically absent reflections) were collected in the hemisphere, $\pm h$, $+ k$, $\pm l$ ($h = -9$ to $+9$, $k = 0$ to 6, $l = -20$ to 20). After deleting the systematically absent reflections from the data set and averaging over equivalent reflections, a total of 1301 unique reflections were used for the structural analysis. Lorentz-polarisation but absorption corrections were applied to the data.

As it was not possible to grow large and proper shaped crystals, some thin circular pellets were prepared from its crushed fine powder at a maximum pressure of $5 \times 10^6\, kg/m^2$ for dielectric constant and loss measurements. These measurements were carried out in the temperature range 77 K to 296 K at two different frequencies, 5 kHz and 10 kHz, using GR 1620 capacitance bridge.

Differential thermal analysis (DTA) and differential scanning calorimetric (DSC) studies have been completed using Sinku–Riko and Perkin–Elmer instruments respectively in the above temperature range on the powder samples. The heating rate in DTA and DSC experiments were 2 and 5 K/min respectively.

3. Analysis and discussion

The Tl and As atoms of TDA were located in the Patterson maps. Positions of all the oxygen atoms were determined using Fourier difference synthesis technique. The hydrogen atom (H) could not be located in the Fourier difference maps calculated on the basis of Tl, As and O positions. This is because of the domination of

the scattering power of Tl and As atoms in the structure. However, the positions of hydrogen atoms were inferred on the basis of hydrogen-bond geometry, isomorphous structures and valancy of the AsO_4 group (as shown in fig. 1). Positional and anisotropic thermal parameters of all the atoms (i.e. Tl, As and O) were refined by full-matrix least-squares methods. The scattering factors for Tl and As atoms were taken from *International tables for X-ray crystallography* (1974) and for oxygen from a computer program package, SHELX 76 (Shetdrick 1976) (which was also used for other calculations). A total of 56 parameters (including scale and extinction) were refined. Final conventioanl R or weighted R factor Rw, (on F) with all the 1301 independent reflections and unit weights was found to be 11%. Though a few weighting (w)-schemes were tried to get approximately constant $w\Delta^2$ $(\Delta = |F_0| - F_c|)$ as small ranges of F_0 and $\sin\theta/\lambda$, unit weight was found to be more appropriate. After removing some weak reflections (i.e. $I > \sigma(F_0)$), remaining 689 unique reflections were used in the refinement and then R-factor went to
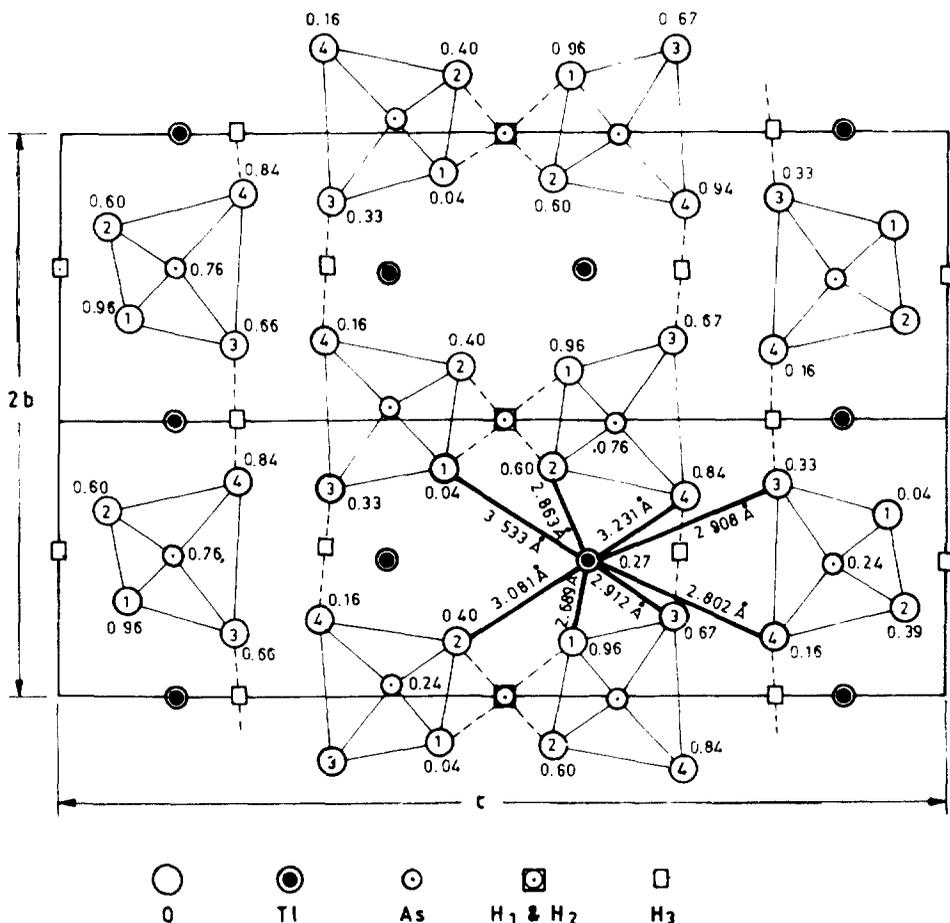

Figure 1. A projection of the crystal structure of TlH_2AsO_4 (showing two unit cells) on to the $b-c$ plane. Atomic heights (in fractional coordinates) are given besides the atoms. The Tl–O coordinations with their distances (Å) are also shown. The hydrogen bonds are shown by dashed lines [for O(1)–H(1)–O(1') and O(2)–H(2)–O(2')]. The designations of the atoms are given inside the circle.

14%. In the final refinement, the shift/e.s.d.'s converged in the third decimal place. Final positional and equivalent isotropic thermal parameters of non-hydrogen atoms are listed in table 1. Some important bond lengths and angles of all the above atoms are given in table 2. Figure 1 shows a projection of the structure of TDA (with two unit cells) onto the a–c plane.

The room temperature crystal structure of TDA was found to be similar to that of CSH_2PO_4 (Choudhary and Nelmes 1978a; Nelmes and Choudhary 1978) and TDP (Nelmes and Choudhary 1981). The As–O distances (table 2) range from 1·642(46) Å to 1·743(48) Å and the O–As–O angles range from 102·4(2·3) to 115·4(2·3)°, indicating that the shape of the AsO_4 tetrahedron is rather regular. The overall structure of the compound can be explained in terms of H-bonded

Table 1. Fractional coordinates of atoms and equivalent isotropic temperature factors, U_{eq} (in Å^2) with e.s.d. in parentheses. The U_{eq} is defined by one-third of the traces of the orthogonal U_{ij} tensor.

atom	x	y	z	U_{eq}
Tl	0·2658(3)	− 0·0033(6)	0·1242(2)	0·041(2)
As	0·7643(6)	0·5200(11)	0·1291(3)	0·026(4)
O(1)	0·9568(79)	0·3459(138)	0·0724(32)	0·062(5)
O(2)	0·6012(56)	0·6676(99)	0·0502(33)	0·047(5)
O(3)	0·6668(46)	0·2471(82)	0·1934(29)	0·036(5)
O(4)	0·8390(53)	0·7266(106)	0·2018(34)	0·025(5)

Table 2. Some important bond lengths (in Å) and bond angles (in degrees) with their e.s.d.'s in parentheses. O(1'), O(2') and O(3') are symmetry related atoms, which participate in hydrogen-bonding.

As–O(2)	1·743(48)
As–O(3)	1·685(39)
As–O(4)	1·716(38)
As–O(1)	1·642(46)
O(1)–O(2)	2·792(3)
O(1)–O(3)	2·586(41)
O(1)–O(4)	2·670(43)
O(2)–O(3)	2·870(40)
O(2)–O(4)	2·665(43)
O(3)–O(4)	2·587(39)
O(1)–H(1)–O(1')	2·586(38)
O(2)–H(2)–O(2')	2·483(43)
O(3)–H(3)–O(3')	2·686(3)
O(2)–As–O(3)	109.1(2.4)
O(2)–As–O(4)	102.4(2.3)
O(2)–As–O(1)	115.4(2.3)
O(3)–As–O(4)	115.2(1.9)
O(3)–As–O(1)	108.3(2.3)
O(4)–As–O(1)	106.7(2.3)

chains of tetrahedra which are continuous along the *a* and *b* axes but discontinuous along the *c*-axis. Tl−O distances and their co-ordinations are shown in figure 1.

Figure 2 shows the variation of dielectric constant of TDA with temperature at two frequencies, 5 kHz and 10 kHz. It has been observed that the dielectric constant of this compound increases continuously with increase of temperature and hence no dielectric anomaly has been detected in the temperature range 77 K to 296 K. Figure 3 shows the variation of dielectric loss of the compounds with temperature and once again no anomaly has been observed in the loss. This type of behaviour in dielectric constant and loss as a function of temperature has already been observed in many other thallium compounds like $TlTaO_3$, $Tl_2Ti_4O_4$, $TlNbO_3$ (Bihan *et al* 1978). This behaviour has been explained as being due to the ionic conductivity as proposed by Schmidt and Parker (1972) in $LiN_2H_5SO_4$, and also by Palau and Lassabatev (1977) in $LiN_2H_5BeF_4$. No proper hysteresis loop has been observed in our study which can support ferro/antiferroelectric behaviour in the present compound. The DTA and DSC curves of the compound (figure 4) do not show any anomalous peak which can support phase transitions of any type.
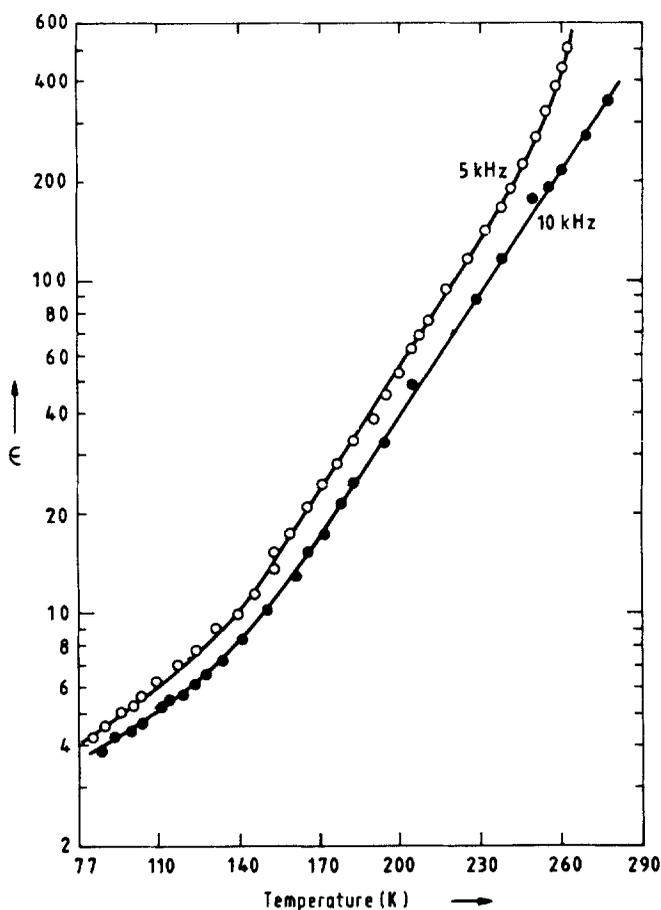

Figure 2. Variation of dielectric constant ϵ as a function of temperature in TDA
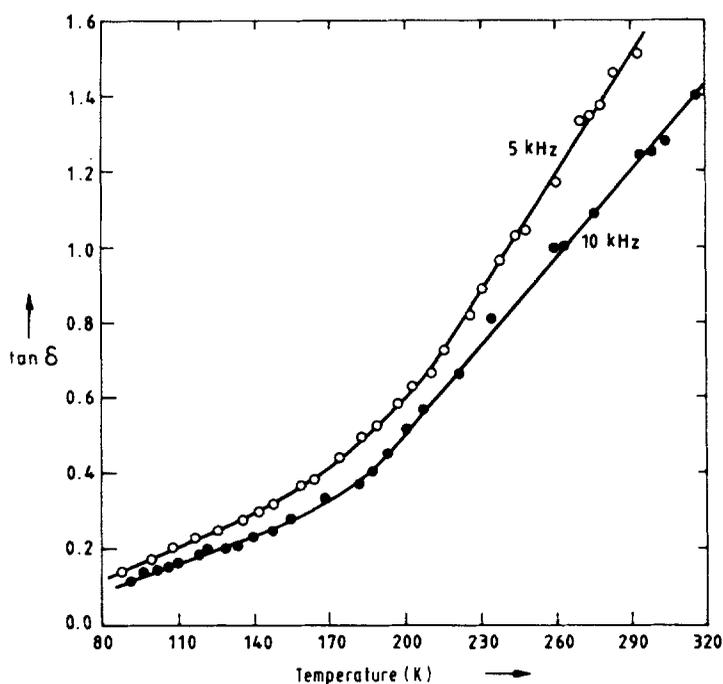
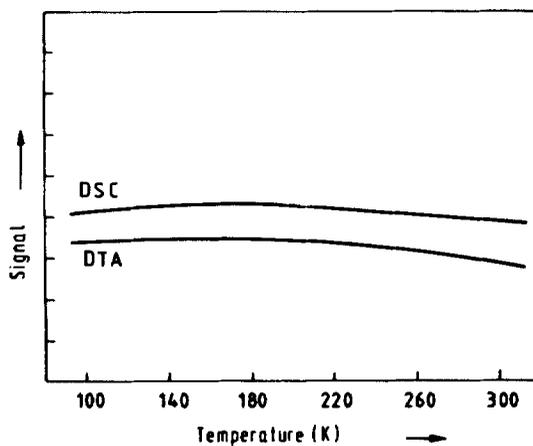**Figure 3.**   Variation of dielectric loss (tan δ) with temperature.

Figure 4.   Signal of DTA and DSC curves as a function of temperature.

Acknowledgements

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