

RAMAN AND INFRARED SPECTROSCOPIC STUDIES OF THE NEW FERROELECTRIC CRYSTAL TELLURIC ACID AMMONIUM PHOSPHATE

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ABSTRACT

Telluric acid ammonium phosphate is a new ferroelectric with its physical properties comparable to that of triglycine sulphate. A detailed spectroscopic study is expected to give information on the nature of ferroelectric phase transition in the crystal. This paper reports for the first time an investigation in the internal mode region to establish the symmetry of the polyatomic groups and their distortion to relate the structure with the ferroelectric behaviour in TAAP.

INTRODUCTION

MONOCLINIC telluric acid ammonium phosphate $[\text{Te}(\text{OH})_6 \cdot 2\text{NH}_4\text{H}_2\text{PO}_4 \cdot (\text{NH}_4)_2\text{HPO}_4]$ belongs to a new class of ferroelectrics with a Curie temperature of 49°C . The room temperature crystal structure of TAAP¹ shows that the space group is Pn with $Z=2$. The main feature in its atomic arrangement may be described as built by an alternation of two types of planes perpendicular to the [101] direction (figure 1). In the first plane there are PO_4 groups and $(\text{NH}_4\text{O})_n$ polyhedra, while in the second set of planes we find TeO_6 groups, NH_4O_n polyhedra and PO_4 groups. All the groups occupy C_1 sites. A vibrational analysis obviously is expected to give more information about the nature of these groups. In this paper we report the preliminary vibrational spectroscopic studies of this crystal.

EXPERIMENTAL

Optical quality single crystals of TAAP were grown at room temperature by water evaporation from the aqueous solution of telluric acid, ammonium dihydrogen phosphate and diammonium hydrogen phosphate taken in the required proportions². The Raman spectra of TAAP were recorded using a Spex-double monochromator with a photon counting system. An argon laser (Spectra-Physics) operating at 4880 Å wavelength with a power output of 200 mW was used to excite the Raman spectra. The mechanical slit width used corresponds to a spectral band pass of 2.5 cm^{-1} . The infrared spectra were recorded in KBr pellets using a Perkin-Elmer 580 model spectrometer.

RESULTS AND DISCUSSION

A factor group analysis taking into account all the atoms including hydrogen will result in 315 internal degrees of freedom after leaving out the three acoustic branches. It will therefore be more appropriate to analyse the vibrational spectrum of this crystal taking into account the nature of the interatomic forces. Here the spectra were analysed in terms of the internal vibrations of the $\text{Te}(\text{OH})_6$, (NH_4^+) , H_2PO_4 and HPO_4 groups and the perturbations caused by the site symmetry. In the first instance and then look for the correlation splitting if any. Theoretically one would expect a large number of lattice vibrations (both due to the translatory and the rotatory types) due to the motion of these 16 polyatomic groups in the unit cell, broadened also by the influence of hydrogens. Experimentally however only a few lines are observed in the low frequency region as shown in figure 2. A detailed analysis of the lattice vibrations to look for a correlation with its ferroelectric behaviour will be

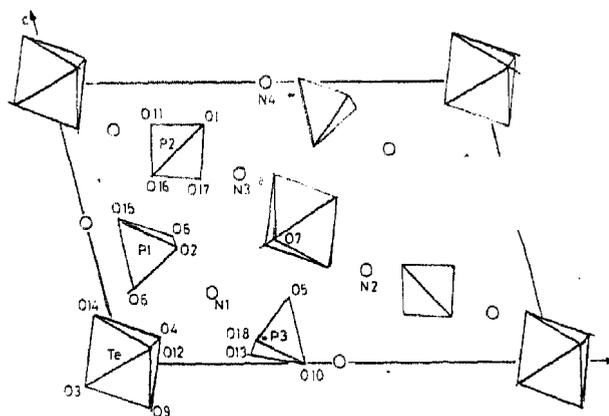


Figure 1. Projection of the atomic arrangement of $\text{Te}(\text{OH})_6 \cdot 2\text{NH}_4\text{H}_2\text{PO}_4 \cdot (\text{NH}_4)_2\text{HPO}_4$ along the b -direction.

* For correspondence,

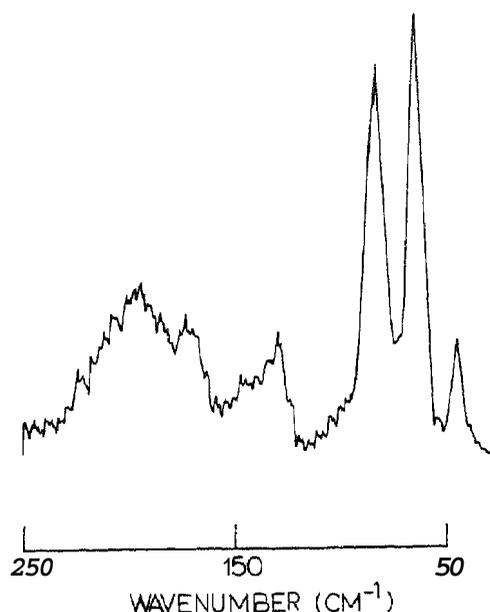


Figure 2. Raman spectra of the low frequency region of TAAP.

carried out separately, Here the internal modes are analysed to establish the symmetry of the polyatomic groups and their distortion to relate the structure with the ferroelectricity in TAAP.

Figure 3 shows the IR spectrum of TAAP while figure 4 shows the Raman spectra of the internal modes.

Te(OH)₆ vibrations

The Te(OH)_6 group consists of vibrations due to TeO_6 octahedron and that of the O-H bonds. The octahedral TeO_6 has six vibrational modes: $\nu_1(A_{1g})$ symmetric stretching, $\nu_2(E_g)$ and $\nu_3(F_{1u})$ asymmetric stretchings, $\nu_4(F_{1g})$ asymmetric bending, $\nu_5(F_{2g})$ symmetric bending and $\nu_6(F_{2u})$ asymmetric bending. While ν_1 , ν_2 and ν_3 are Raman active, ν_3 and ν_4 are IR active. ν_6 is inactive both in IR and Raman

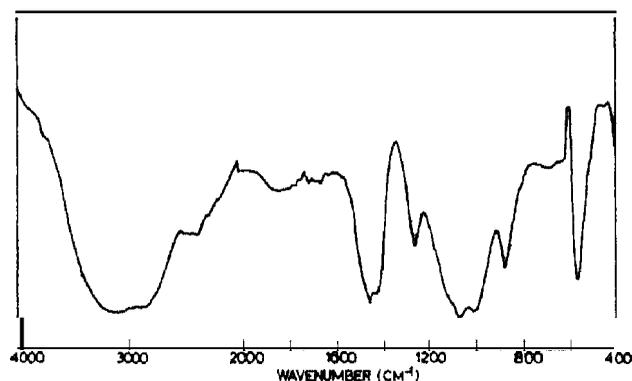


Figure 3. Infrared spectra of internal mode region of TAAP.

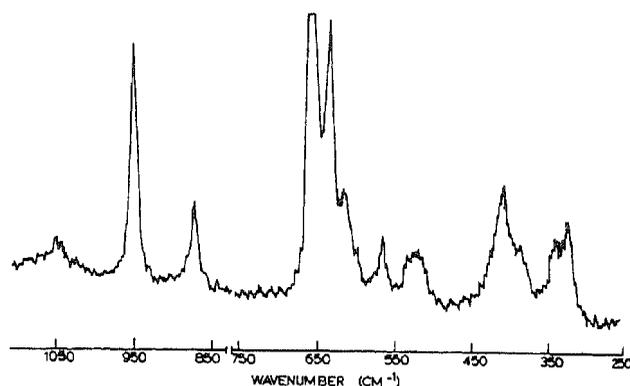


Figure 4. Raman spectra of internal mode region of TAAP.

spectra. The TeO_6 symmetric stretching (ν_1) vibration is expected at $600\text{--}700\text{ cm}^{-1}$. The very strong line at 653 cm^{-1} in the Raman spectrum is therefore assigned to this vibration. The doubly degenerate asymmetric stretching vibration (ν_2) is split into two lines and are observed at 610 and 632 cm^{-1} . The asymmetric and symmetric bending modes ν_4 and ν_5 are observed in the region $300\text{--}350\text{ cm}^{-1}$. The asymmetric stretching mode (ν_3) vibration and asymmetric bending vibration by O-P-O of H_2PO_4^- and HPO_4^{2-} lie in the same region and could not be identified unambiguously. It can be noticed that none of these lines are observed in IR spectra.

Phosphate group vibrations

The P-O(H) stretching vibrations of HPO_4^{2-} and H_2PO_4^- are expected³ in the region $800\text{--}1000\text{ cm}^{-1}$. The Raman lines observed at 948 and 878 cm^{-1} , and the IR lines observed at 850 , 970 cm^{-1} are attributed to these vibrations. The Raman lines observed at 1048 , 1060 cm^{-1} and in IR at 1040 cm^{-1} correspond to the P-O stretching vibrations of HPO_4^{2-} and H_2PO_4^- . A line at 1230 cm^{-1} in IR is attributed to the P-O-H bending vibrations of the two phosphate groups. The lines observed in the Raman spectra in the region $382\text{--}410\text{ cm}^{-1}$ and $510\text{--}560\text{ cm}^{-1}$ are due to the asymmetric, symmetric and OPO bending mode vibrations. The O-H stretch is observed in the region $2600\text{--}3300\text{ cm}^{-1}$.

NH₄ group vibrations

The NH_4^+ ion is a tetrahedron having four vibrational modes and all the four appear in Raman and IR spectra due to its general position in the crystal. The symmetric and asymmetric stretching modes ν_1 and ν_3 appear as broad bands in the region $2800\text{--}3300\text{ cm}^{-1}$ along with the O-H vibrations of

Table 1 Vibrational frequencies of internal modes and their assignment to different groups

Raman	IR	Assignment
cm ⁻¹	cm ⁻¹	
320	-	$\nu_4(\text{TeO}_6)$ &
340		$\nu_5(\text{TeO}_6)$
382		OPO asy. bending modes of
410	-	H_2PO_4^- , HPO_4^-
520		OPO sy. bending modes
535	540	of H_2PO_4^- ,
564		HPO_4^- & $\nu_3(\text{TeO}_6)$
610		
632		$\nu_2(\text{TeO}_6)$
653		$\nu_1(\text{TeO}_6)$
878	850	P-O(H) stretching vib. of
948	970	H_2PO_4^- , HPO_4^-
1048	1040	P-O stretching vib. of HPO_4^- ,
1060		H_2PO_4^-
1410	1390	
		$\nu_4(\text{NH}_4^+)$
1436	1440	
1682	1640	
		$\nu_2(\text{NH}_4^+)$
1789	1690	
2600	2400	ν_1 & $\nu_3(\text{NH}_4^+)$
to	to	& $\nu(\text{N-H-O})$
3300	3400	stretching mode.

other groups present. The symmetric bending mode appears as two lines in the region 1682–1780 cm⁻¹ in Raman and 1640–1690 cm⁻¹ in IR. The asymmetric bending mode appears at 1410 and 1436 cm⁻¹ in Raman, and at 1390 and 1440 cm⁻¹ in IR. Table 1 shows the different frequencies observed in Raman and IR spectra and their assignment to different groups.

The structural analysis of this crystal¹ indicates that the PO₄ tetrahedron is distorted with relatively

large deviations in the P–O distances from the average values. These deviations have been suggested to be due to the possible presence of hydrogen bonds. The bands observed both in IR and Raman corresponding to the asymmetric bending mode of NH₄⁺ show an upward shift of as much as 39 cm⁻¹ from the free ion frequency 1397 cm⁻¹. This as well as the presence of a broad band in the region 2600–3300 cm⁻¹ in Raman and IR confirms the existence of hydrogen bonds of the type N–H–O corresponding to the N–O distances reported in the crystal structure.

The temperature variation of internal modes across the phase transition has been studied to look for any change in the spectra as a result of phase transition. However no significant changes have been observed. The resemblance of the properties of TAAP with TGS⁴ predicts interesting temperature behaviour of lattice modes⁵. The detailed studies of polarized Raman spectra and the temperature variation of lattice modes and hydrogen bond region are in progress.

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