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Raman and infrared spectral analysis of thallium niobyl phosphates: $Tl_2NbO_2PO_4$, $Tl_3NaNb_4O_9(PO_4)_2$ and $TlNbOP_2O_7$

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Abstract

Raman and infrared spectra of $Tl_2NbO_2PO_4$, $Tl_3NaNb_4O_9(PO_4)_2$ and $TlNbOP_2O_7$ are reported. The observed bands are assigned in terms of vibrations of NbO_6 octahedra and PO_4 tetrahedra in the first two compounds and in terms of NbO_6 octahedra and $P_2O_7{}^{4-}$ anion in the third compound. The NbO_6 octahedra in all the title compounds are found to be corner-shared and distorted. The higher wavenumber values of the ν_1 (NbO_6) mode and other stretching modes indicate that the NbO_6 octahedra in them are distorted in the order $TlNbOP_2O_7 > Tl_2NbO_2PO_4 > Tl_3NaNb_4O_9(PO_4)_2$. The splitting of the ν_3 (PO_4) mode indicates that PO_4 tetrahedra is distorted more in $Tl_2NbO_2PO_4$ than in $Tl_3NaNb_4O_9(PO_4)_2$. The symmetry of $P_2O_7{}^{4-}$ anion in $TlNbOP_2O_7$ is lowered. Bands indicate that the P–O–P bridge in the above compound has a bent P–O–P bridge configuration. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Raman spectra; IR spectra; Niobyl phosphates; NbO_6 octahedra; PO_4 tetrahedra; $P_2O_7{}^{4-}$ anion

1. Introduction

In recent years there has been great interest in compounds with ion-exchange properties, for technological applications. The luminescence of phosphatoniobates strongly depends on crystal structure and consequently it is of interest to get precise structural information of these related compounds [1]. Structure of such crystals, $Tl_2NbO_2PO_4$, $Tl_3NaNb_4O_9(PO_4)_2$ and $TlNbOP_2O_7$, have been reported by Fakhfakh et al. [2–4]. In this paper, an attempt is made to analyse the vibrational spectra of the three thallium niobyl phosphates to get an insight into their structure.

2. Experimental

The samples for the present study were prepared by the method described by Fakhfakh et al. [2–4]. Raman spectra of all the three compounds were recorded using a SPEX 1401 Raman Spectrometer with a resolution better than 3 cm^{-1} at room temperature. Spectra were recorded using both 514.5 and 488.0 nm lines of a Spectra Physics 165 Model Argon ion laser. The intensity of the bands of $Tl_3NaNb_4O_9(PO_4)_2$ and $TlNbOP_2O_7$ was weak in the spectra. Therefore, Raman spectra were again recorded using DILOR MICRODIL 28 Raman spectrometer (514.5 nm) and DILOR Z 24 Raman spectrometer (488.0 nm). FTIR spectra of the samples were recorded in the 400–1400 cm^{-1} region using an FTIR-NICOLET 205 X spectrometer by the KBr pellet method and in the 50–400 cm^{-1} region using a Bruker IFS 66v Spectrometer by the polyethylene pellet method.

3. Factor group analysis

$Tl_2NbO_2PO_4$ crystallizes in the rhombohedral system with 6 formula units per Bravais cell in the space group R3. The unit cell parameters are $a = 8.746(2)$ and $c = 44.753(7)$ Å. The irreducible representation of the sample at $k = 0$ excluding the acoustic modes is given by [6]

$$\Gamma_{177} = 30A_g + 30E_g + 29A_u + 29E_u$$

The $Tl_3NaNb_4O_9(PO_4)_2$ crystallizes into the orthorhombic system with space group C2cm, with $a = 9.891$, $b = 21.298$ and $c = 7.346$ Å [3]. It contains 2 formula units per Bravais cell. The following irreducible representation will give the modes at $k = 0$:

$$\Gamma_{159} = 41A_1 + 39A_2 + 41B_1 + 38B_2$$

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The $TlNbOP_2O_7$ crystallizes in the monoclinic system with space group P21/n and with 2 formula units per Bravais cell [4,5]. The irreducible representation obtained at $k = 0$ is

$$\Gamma_{69} = 15A_g + 20A_u + 15B_g + 19B_u$$

4. Results and discussion

4.1. $Tl_2NbO_2PO_4$

4.1.1. Vibrations of NbO_6 octahedra

The structure of $Tl_2NbO_2PO_4$ is built up from layers of NbO_6 octahedra and PO_4 tetrahedra sharing corners. The Nb atom is off-centered within this octahedron, thus leading to a long Nb–O distance Nb–O(8), 2.24 Å, and a short one Nb–O(5), 1.73 Å, corresponding to the unshared oxygen. The four remaining Nb–O distances range from 1.92, 1.96, 2.07 to 2.09 Å. The first two relate to Nb–O–Nb and the latter two to Nb–O–P(1) or P(3) bonds [2]. In metal oxide systems containing niobium, titanium or tungsten, the binding forces within the metal–oxygen octahedra are large compared to crystal binding forces. The internal vibrations of the MO_6 group in solids are quite close to the free-ion modes. The external modes occur at considerably lower frequencies than the internal modes [7]. An octahedron with O_h symmetry has six fundamental vibrations, the symmetric stretching mode ν_1 (A_{1g}), asymmetric stretching modes ν_2 (E_g) and ν_3 (F_{1u}), asymmetric bending mode ν_4 (F_{1u}) and symmetric bending mode ν_5 (F_{2g}), and the inactive mode ν_6 (F_{2u}). The ν_1, ν_2 and ν_5 modes are Raman active while ν_3 and ν_4 modes are IR active. The ν_6 mode is inactive in both the IR and Raman [8–13]. The Nb^{5+} ion is too small to form regular NbO_6 octahedra. In most of the oxide systems, its O_h symmetry is found to be lowered due to distortion [7]. Depending on the extent of distortion, the NbO_6 octahedra can have any of the five symmetries, viz D_{4h}, D_{3d}, C_{4v}, C_{3v} or C_{2v} [7].

The Nb–O stretching modes are usually observed in the 580–890 cm^{-1} region [14]. In Raman spectra (Fig. 1a), an intense band at 868 cm^{-1} and two moderately intense bands at 904 and 833 cm^{-1} are obtained (Table 1). In the IR spectrum a moderately intense band is observed at 858 cm^{-1} (Fig. 3a). These bands are assigned to the symmetric Nb–O stretching modes (ν_1). The ν_2 (E_g) mode is IR inactive while ν_3 (F_{1u}) mode is IR active. A very intense band which splits into two (716 and 728 cm^{-1}) is observed in the IR. A moderately intense band (712 cm^{-1}) is obtained in this region in the Raman spectrum. They are assigned to the ν_3 modes. Raman bands due to the ν_2 (E_g) mode of a perfect NbO_6 octahedra are weak since Nb^{5+} ion with d^0 configuration participates significantly in π-bonding [15,16]. Raman bands (Fig. 1a) around 633 cm^{-1} and IR bands around 622 cm^{-1} (Fig. 3a) are assigned to the ν_2 modes. The ν_4 mode of NbO_6 octahe-

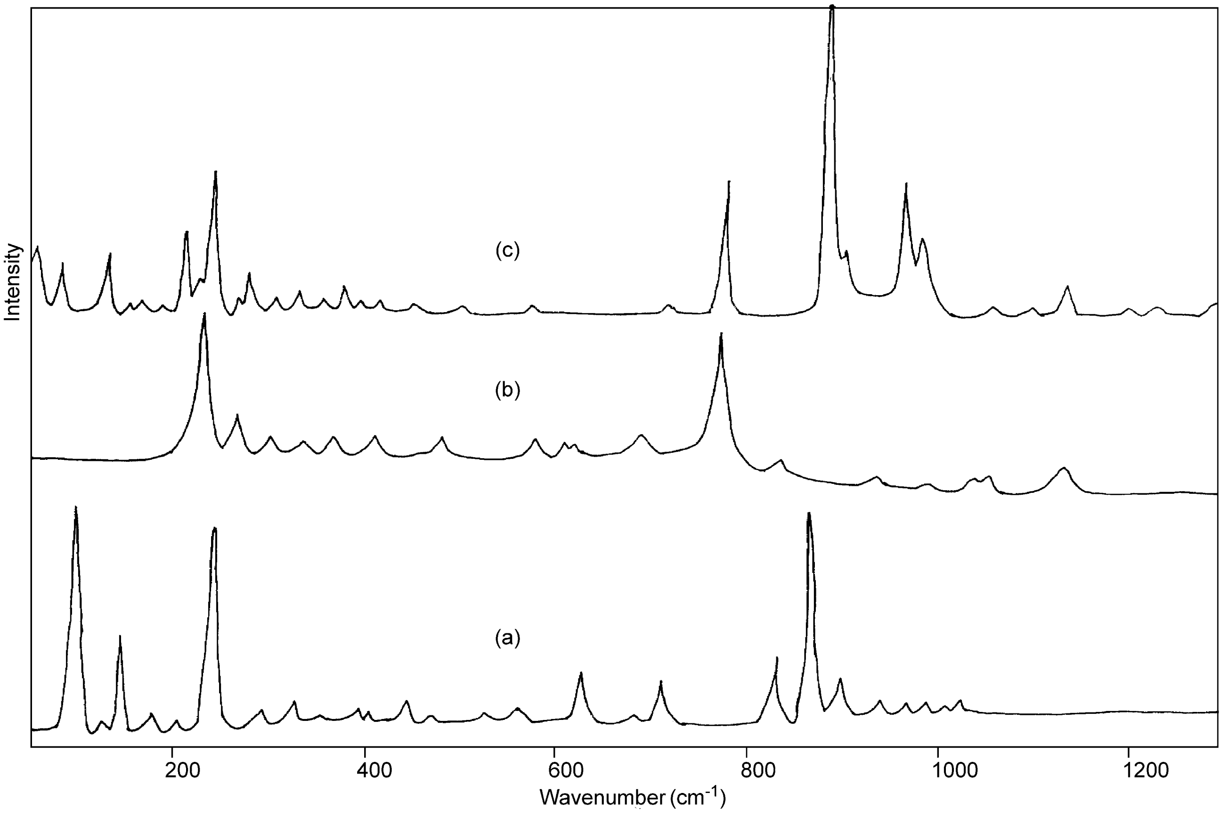

Fig. 1. Raman spectra of (a) $Tl_2NbO_2PO_4$, (b) $Tl_3NaNb_4O_9(PO_4)_2$ and (c) $TlNbOP_2O_7$ in the region 50–1300 cm^{-1}.

Table 1
Spectral data (cm^{-1}) and band assignments $Tl_2NbO_2PO_4$ and $Tl_3NaNb_4O_9(PO_4)_2$[a]

$Tl_2NbO_2PO_4$		$Tl_3NaNb_4O_9(PO_4)_2$		
Raman	FTIR	Raman	FTIR	Assignments
	65 m			
100 vs	109 m		106 m	
127 vw	135 vw			
145 ms	171 w		167 m	External modes
180 w	195 vw			
205 w	209 vw		205 m	
240 vs	234 w	233 s		Tl–O
	260 s	272 ms	264 w	ν_6NbO_6
291 w	290 m			
327 w		305 w	303 m	
		345 vw		ν_5NbO_6
369 vw	368 sh	370 w	373 m	
397 w	392 vs			
401 w		412 w	430 vw	$\nu_2PO_4^{3-}$
446 w	442 s		452 w	ν_4NbO_6
470 vw		488 w		
527 vw	558 s		538 vs	$\nu_4PO_4^{3-}$
			550 vs	
565 w	564 sh	578 w	557 vs	
			579 vs	
633 w	622 m	611 w		ν_2NbO_6
681 w		626 sh		
712 mbr	716 vs	698 wbr		ν_3NbO_6
	728 sh			
833 m		786 s	762 w	
868 s	858 m	832 w	855 m	ν_1NbO_6
904 w				
941 w	939 s	930 vw	933 s	$\nu_1PO_4^{3-}$
966 w	964 vs		979 vs	
981 w		988 w	1001 sh	
1005 w				
1025 w	1053 m	1039 m	1039 ms	$\nu_3PO_4^{3-}$
	1100 vw	1051 sh		
	1137 w	1129 m	1111 s	

[a] vw: very weak; w: weak; m: medium; wbr: weak and broad; sh: shoulder; vs: very strong; s: strong; ms: moderately strong.

dra falls in the region of bending modes of the PO_4 tetrahedra. Therefore, an unambiguous assignment of these bands is not possible. The bands in the 370–320 cm^{-1} region are due to the ν_5 modes. In the region of the inactive mode ν_6, a very intense band at 240 cm^{-1} is obtained in Raman spectra. In the IR spectra also bands are observed in this region with a moderately intense band at 290 cm^{-1} (Fig. 2a). The high intensity of the band at 240 cm^{-1} is probably due to the fact that the T1–O modes also occur in the same region [17].

In crystals having edge-shared octahedra, Raman bands are obtained around 998 cm^{-1}. If corner-shared octahedra are present, bands are observed around 884 cm^{-1} [18]. In the present study, an intense Raman band is obtained at 868 cm^{-1} with a few weak bands at 833 and 904 cm^{-1}. This confirms the presence of corner-shared octahedra in the crystal [2]. The appearance of multiple bands in the non-degenerate ν_1 mode region is due to the Nb–O bonds of varying strengths as observed in the X-ray studies [2]. The band at 904 cm^{-1} can be assigned to the shortest Nb–O bond of length 1.73 Å [19]. The non-appearance of this band in the IR spectra confirms that this band is due to the Nb–O symmetric stretching mode. In crystals containing MoO_6 octahedra, Hardcastle and Wachs [20] have formulated the following empirical relation connecting the Mo–O bond lengths and Raman scattering frequencies [20].

$$\nu\ (\mathrm{cm}^{-1}) = 32895 \exp(-2.073R)$$

where R is the Mo–O bond length. Substitution of the value of 1.73 Å, the shortest Nb–O bond length in the NbO_6 octahedra gives a value of 911 cm^{-1}. The band at 904 cm^{-1} is obtained in the present study in agreement with Hardcastle's relation. The presence of Raman active modes (ν_1, ν_2 and ν_5) in the IR spectra and the activation of ν_6 mode both in the Raman and IR spectra is in agreement with high distortion of the NbO_6 octahedra and lowering of its symmetry from O_h to a lower one (C_{4v} or C_{3v} or C_{2v}). For lower symmetries (C_{4v}, C_{3v}, C_{2v}), ν_1, ν_2, ν_5 and ν_6 modes are both Raman and IR active [7–11].

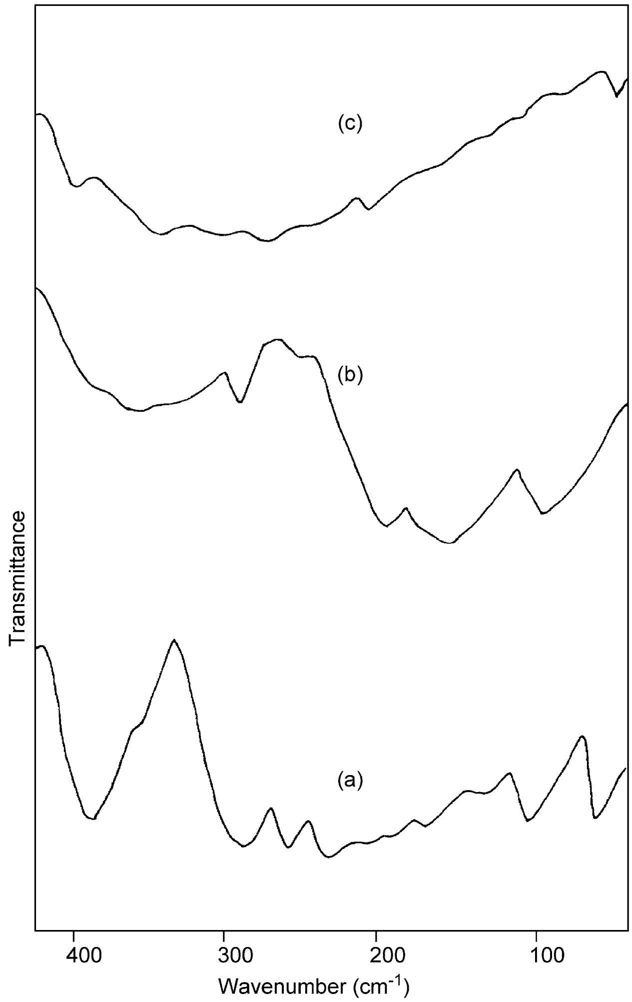

Fig. 2. FTIR spectra of (a) $Tl_2NbO_2PO_4$, (b) $Tl_3NaNb_4O_9(PO_4)_2$ and (c) $TlNbOP_2O_7$ in the region 50–400 cm^{-1}.

4.1.2. PO_4^{3-} *vibrations*

A free PO_4 tetrahedra with T_d symmetry has four internal modes of vibration, ν_1 (A_1) 938, ν_2 (E) 420 cm^{-1}, ν_3 (F_2) 1017 cm^{-1} and ν_4 (F_2) 567 cm^{-1}. All the above modes are Raman active while ν_3 and ν_4 alone are IR active [9,11,12]. In the symmetric stretching mode (ν_1) region of PO_4 tetrahedra, three distinct bands are observed at 941, 966 and 981 cm^{-1}. In the IR spectrum also two strong bands are observed at 939 and 964 cm^{-1}. The triply degenerate asymmetric stretching mode region consists of three bands in the IR at 1053, 1100 and 1137 cm^{-1}. Corresponding Raman bands are observed at 1005 and 1025 cm^{-1}. The detailed assignments of bands to different modes are given in Table 1. The appearance of the three distinct peaks in the non-degenerate symmetric stretching region of the PO_4 tetrahedra is due to the presence of different P–O distances in the crystal [2]. X-ray structure studies reveal that one of the PO_4 tetrahedra is nearly regular while the other two are distorted. The band at 981 cm^{-1} having a higher wavenumber value is due to the shortest P–O bond length of 1.49 Å in the distorted PO_4 tetrahedra.

4.2. *$Tl_3NaNb_4O_9(PO_4)_2$*

4.2.1. *Vibrations of NbO_6 octahedra*

The crystal structure is built up of NbO_6 octahedra sharing all their vertices with either octahedron or PO_4 tetrahedron. All PO_4 tetrahedra share three of their vertices with three octahedra, the fourth one being unshared. They form chains along ‘*c*’-axis. These chains are connected together by isolated NbO_6 octahedra leading to a three-dimensional network, which delimits cavities and tunnels, occupied by the Tl^+ and Na^+ ions. The off-centered position of Nb results in the distortion of the octahedra leading to different Nb–O distances, the shortest being 1.83 Å Nb(2)–O(4) and the longest 2.15 Å Nb(2)–O(5). Each oxygen atom is bonded either to two Nb atoms or to one Nb atom and one P atom.

Bands obtained in the Raman spectrum of the crystal are generally weak compared to the bands obtained for $Tl_2NbO_2PO_4$ (Fig. 1b). A fairly intense band in the Raman spectrum (DILOR MICRODIL 28) at 786 cm^{-1} and the weak band at 832 cm^{-1} can be assigned to the ν_1 mode of NbO_6 octahedra (Table 1). In the IR spectrum a fairly intense band is observed at 855 cm^{-1}. The very weak band observed at 698 cm^{-1} (Raman) is assigned to the Raman inactive ν_3 mode. A shoulder can be observed in this region in the strong broad band extending from 700 to 430 cm^{-1} obtained in the IR spectrum (Fig. 3b). The bands near 611 cm^{-1} in both the spectra can be assigned to the ν_2 mode. The assignment of the bending mode ν_4 is difficult as it falls in the bending mode region of PO_4 tetrahedra. The inactive ν_6 mode gives a fairly intense Raman band at 233 cm^{-1} in this crystal also. Appearance of distinct peaks in the Raman spectra in the symmetric Nb–O stretching region confirms the presence of different Nb–O bond lengths in the crystal [3]. The wavenumber values of the ν_1 mode are below 900 cm^{-1} and this is in agreement with corner-shared NbO_6 octahedra present in the crystal [3,18].

4.2.2. PO_4^{3-} *vibrations*

Raman bands attributed by the PO_4 stretching modes are usually found to be weak in most of the metal oxide systems like $KTiOPO_4$, $SbOPO_4$, $MoPO_5$, $NbOPO_4$, etc. [7,9,12,21–23] due to the presence of –M–O–M chains. In $Tl_3NaNb_4O_9(PO_4)_2$ also the phosphate bands in Raman spectra are weak as observed earlier in $Tl_2NbO_2PO_4$ (Fig. 1a and b). Assignments of the bands are given in Table 1. The appearance of different bands in the non-degenerate stretching mode (ν_1) region is in agreement with the different P–O bond lengths determined from X-ray studies [3]. The splitting of the ν_3 mode of PO_4 tetrahedra is 72 cm^{-1} in $Tl_3NaNb_4O_9(PO_4)_2$ and 84 cm^{-1} in $Tl_2NbO_2PO_4$. This observation suggests that the distortion of PO_4 tetrahe-

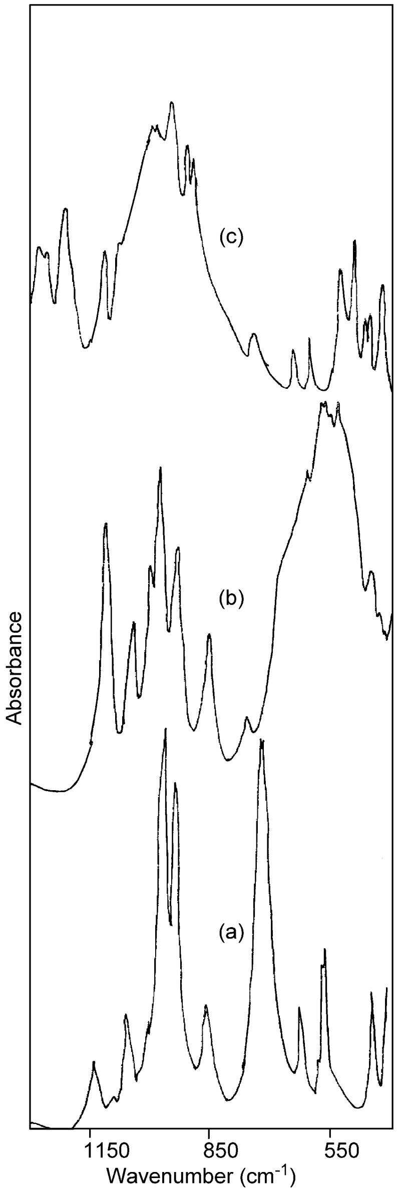

Fig. 3. FTIR spectra of (a) $Tl_2NbO_2PO_4$, (b) $Tl_3NaNb_4O_9(PO_4)_2$ and (c) $TlNbOP_2O_7$ in the region 400–1400 cm^{-1}.

dra in the $Tl_2NbO_2PO_4$ is slightly higher than that in $Tl_3NaNb_4O_9(PO_4)_2$.

4.3. $TlNbOP_2O_7$

In $TlNbOP_2O_7$, the three-dimensional $[NbOP_2O_7{}^-]_n$ framework is built up of NbO_6 octahedra and P_2O_7 diphosphate groups sharing corners. The NbO_6 octahedra are linked together through five of its vertices, to five PO_4 tetrahedra belonging to five different P_2O_7 groups. Its sixth vertex O(7) is unshared and points into the large tunnel delimited by the framework and running along ‘*a*’. Each P_2O_7 group is linked to five NbO_6 octahedra and has one unshared vertex O(6), as does O(7), points into the tunnel where the Tl^+ ions are situated [4].

4.3.1. *Vibrations of* NbO_6 *octahedra*

The most intense band in Raman spectrum of the title compound is at 892 cm^{-1} and it has a shoulder at 907 cm^{-1} (Fig. 1c). Intense bands are also obtained in the IR at 886 and 900 cm^{-1} (Fig. 3c). These are assigned to the symmetric stretching ν_1 mode of NbO_6 octahedra. The moderately intense Raman band at 787 cm^{-1} is also assigned to the symmetric Nb–O stretching vibration and it corresponds to Nb–O bonds of longer bond lengths. No IR band is observed corresponding to the above band. The ν_2, ν_3, ν_4 and ν_5 modes of NbO_6 octahedra cannot be assigned unambiguously as the PO_3 and P–O–P modes also fall in the same region. However, a few of them are assigned in comparison with the bands observed in $Rb_2(VO)_3(P_2O_7)_2$ and $(VO)_2P_2O_7$ [24,25], as VO_6 octahedra and P_2O_7 exist in them as NbO_6 and P_2O_7 exist in the title compound. The IR and Raman inactive ν_6 mode is obtained in both IR and Raman spectra in the same region as in $Tl_2NbO_2PO_4$ and $Tl_3NaNb_4O_9(PO_4)_2$. An intense Raman band is obtained at 248 cm^{-1} as in $TlNbOPO_4$ due to the presence of Tl–O modes in the same region (Fig. 1c) [17].

Bands around 900 cm^{-1} in the Raman spectra corresponding to the ν_1 mode of NbO_6 octahedra confirm the presence of corner-shared octahedra suggested by X-ray diffraction studies [4]. Appearance of multiple bands also confirms the presence of different Nb–O bond lengths. Higher wavenumber values of this mode indicate that the NbO_6 octahedra in the crystal are distorted [9,20,26,27]. The appearance of the inactive ν_6 mode in both IR and Raman also confirms the distortion of the octahedra. From the appearance of stretching modes in the higher wavenumber side, the NbO_6 octahedra is found to be distorted more in $Tl_2NbO_2PO_4$ and $TlNbOP_2O_7$ than in $Tl_3NaNb_4O_9(PO_4)_2$. Further, the appearance of a moderately intense band in the ν_2 mode region of the Raman spectra of $Tl_2NbO_2PO_4$ substantiates the above conclusion.

4.3.2. $P_2O_7{}^{4-}$ *vibrations*

The assignment of bands of $P_2O_7{}^{4-}$ ions is carried out in terms of PO_3 and P–O–P group vibrations. The P–O–P stretching modes in $P_2O_7{}^{4-}$ are expected to be at lower wavenumbers than those of terminal P–O stretching modes in the 1250–975 cm^{-1} region [24,28]. The symmetric stretching terminal P–O modes give moderately intense bands in the Raman spectra at 971 and 993 cm^{-1}. In the IR intense bands are obtained at 973 and 993 cm^{-1}. The intense IR bands in the 1100–1270 cm^{-1} region are assigned to the $\nu_{as}PO_3$ modes. The very intense band at 939 cm^{-1} in the IR spectra is due to IR active ν_{as}P–O–P mode. In the region of ν_sP–O–P vibration, a very weak

Table 2
Spectral data (cm^{-1}) and assignments of $TlNbOP_2O_7$[a]

Raman	IR	Assignments
69 m	52 vw	
89 m	69 w	
	103 w	
126 vw	132 w	
143 vw		External modes
156 vw	154 w	
168 vw		
197 vw		
221 s	225 w	ρPO_3
234 sh		
248 vs	248 w	Tl–O
275 w	263 w	$\nu_6 NbO_6$
283 m	289 w	
312 w	321 w	$\nu_5 NbO_6$ and δP–O–P
346 w		
358 w		
373 w	361 w	$\nu_5 NbO_6$
400 w		
420 w	417 w	
459 vw	447 w	$\nu_s PO_3$ and $\nu_4 NbO_6$
	460 w	
506 vw	490 m	$\delta_s PO_3$
	520 m	$\delta_{as} PO_3$
587 vw	593 m	$\nu_2 NbO_6$
	636 m	$\nu_3 NbO_6$
721 vw	730 w	ν_sP–O–P
	746 sh	
787 ms		
892 vs	886 s	$\nu_1 NbO_6$
907 sh	900 s	
	939 vs	
971 ms	973 s	ν_{as}P–O–P
993 m	993 s	$\nu_s PO_3$
1066 vw	1066 sh	$\nu_{as} PO_3$
1101 w		
1143 w	1103 s	
1204 vw	1206 vs	
1238 vw	1248 vs	
1299 vw	1270 sh	

[a] vw: very weak; w: weak; m: medium; wbr: weak and broad; sh: shoulder; vs: very strong; s: strong; ms: moderately strong.

band is obtained in Raman at 721 cm^{-1} and a weak band at 731 cm^{-1} in the IR. Band assignments are given in Table 2.

Multiple bands obtained in the symmetric and asymmetric stretching mode region of PO_3 group in both Raman and IR spectra confirm different terminal P–O bond lengths in the crystal [4]. Further, the appearance of multiple bands in the PO_3 region of the spectra (IR and Raman) is attributed to the lowering of symmetry of $P_2O_7^{4-}$ ion. For a linear P–O–P bridge, ν_sP–O–P is observed only in Raman. But this mode is active in both Raman and IR for a bent bridge configuration [24]. The presence of ν_sP–O–P bands both in the Raman and IR suggests a bent P–O–P bridge configuration. The above result is further confirmed by the appearance of ν_{as}P–O–P bands at a lower wavenumber than the PO_3 stretching modes. Due to the bent bridge configuration of the P–O–P bridge, the symmetry is lowered from dihedral to a lower one [28].

5. Conclusions

The NbO_6 octahedra in all the title compounds are found to be corner-shared and distorted. From the appearance of stretching modes in the higher wavenumber side, the NbO_6 octahedra is found to be distorted more in $Tl_2NbO_2PO_4$ and $TlNbOP_2O_7$ than in $Tl_3NaNb_4O_9(PO_4)_2$. Further, the appearance of a moderately intense band in the ν_2 mode region of the Raman spectra of $Tl_2NbO_2PO_4$ substantiates the above conclusion. The splitting of the ν_3 mode of PO_4 tetrahedra is 72 cm^{-1} in $Tl_3NaNb_4O_9(PO_4)_2$ and 84 cm^{-1} in $Tl_2NbO_2PO_4$. This observation suggests that the distortion of PO_4 tetrahedra in the $Tl_2NbO_2PO_4$ is slightly higher than that in $Tl_3NaNb_4O_9(PO_4)_2$. The symmetry of $P_2O_7^{4-}$ anion in $TlNbOP_2O_7$ is lowered. Bands indicate that the P–O–P bridge in the above compound has a bent P–O–P bridge configuration.

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