

INFRARED AND RAMAN SPECTRA OF MAGNESIUM AMMONIUM PHOSPHATE HEXAHYDRATE (*STRUVITE*) AND ITS ISOMORPHOUS ANALOGUES. X. VIBRATIONAL SPECTRA OF MAGNESIUM RUBIDIUM ARSENATE HEXAHYDRATE AND MAGNESIUM THALLIUM ARSENATE HEXAHYDRATE

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Polycrystalline samples of struvite-type $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ in both protiated and deuterated forms have been prepared for the first time by a precipitation method. Detailed analysis of their infrared (IR) and Raman (R) spectra recorded at room temperature (RT) and liquid nitrogen temperature (LNT) has been carried out and assignment of the vibrational bands has been proposed. The observed spectral pictures confirm the isostructurality of the two arsenate salts in agreement with the structural data. Similarly to other struvite-type and structure-related arsenate salts, the $\nu_1(\text{AsO}_4)$ modes appear at higher frequencies than the $\nu_3(\text{AsO}_4)$ vibrations. Low intensity and temperature sensitive bands that could be assigned as due to stretching Mg-O vibrations and $\nu_4(\text{AsO}_4)$ modes are observed below 500 cm^{-1} in the LNT IR spectra of the studied compounds, at 472 cm^{-1} and 445 cm^{-1} for the rubidium analogue and at 470 cm^{-1} and 440 cm^{-1} for the thallium analogue. In the far-infrared and Raman spectra many bands are observed between 400 cm^{-1} and 200 cm^{-1} , most of which are sensitive to deuteration, suggesting that they are not pure but coupled and can be related to $\nu(\text{Mg-Ow})$ modes. On the other hand, a band around 405 cm^{-1} in the spectra of the protiated compounds most probably is due to $\nu_2(\text{AsO}_4)$ mode because of its frequency position, intensity and slight sensitivity to deuteration.

Keywords: magnesium rubidium arsenate hexahydrate; magnesium thallium arsenate hexahydrate; infrared spectra; Raman spectra

ИНФРАЦРВЕН И РАМАНСКИ СПЕКТАР НА МАГНЕЗИУМ-АМОНИУМ-ФОСФАТ-ХЕКСАХИДРАТ (*СТРУВИТ*) И НЕГОВИТЕ ИЗОМОРФНИ АНАЛОЗИ. X. ВИБРАЦИОНАЛНИ СПЕКТРИ НА МАГНЕЗИУМ РУБИДИУМ АРСЕНАТ ХЕКСИДРАТ И МАГНЕЗИУМ ТАЛИУМ АРСЕНАТ ХЕКСИДРАТ

Подготвени се за прв пат поликристални примероци од типот на струвит $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ и $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ во протонирани и во деутерирани форми со методот на таложење. Извршена е детална анализа на нивните инфрацрвени (IR) спектри, снимени на собна температура и на температурата на вриење на течен азот, и рамански (R) спектри снимени на собна температура и предложена е нивна асигнација. Добиените спектри ја потврдуваат изоструктурноста на двете арсенатни соли, што е во согласност со структурните податоци. Слично на другите арсенатни соли од струвитен тип и од струвитно сродни типови на структура, модовите на $\nu_1(\text{AsO}_4)$ се појавуваат

на повисоки фреквенции од $\nu_3(\text{AsO}_4)$. Лентите со послаб интензитет кои се температурно осетливи, а во инфрацрвените спектри снимени на ниски температури се забележани под 500 cm^{-1} , може да се припишат на валентни Mg–O вибрации и на модови на $\nu_4(\text{AsO}_4)$, на 472 cm^{-1} и 445 cm^{-1} за рубидиумовиот аналог и на 470 cm^{-1} и 440 cm^{-1} за талиумовиот аналог. Во спектрите снимени во далечната инфрацрвена област и во раманските спектри се забележуваат многу ленти помеѓу 400 cm^{-1} и 200 cm^{-1} , од кои повеќето се чувствителни на деутерирање, што сугерира дека тие не се чисти, туку спрегнати и можат да бидат поврзани со модовите на $\nu(\text{Mg–Ow})$. Од друга страна, поради нејзината фреквенција, интензитет и мала чувствителност на деутерирање, лентата на околу 405 cm^{-1} во спектарот на протонираните соединенија најверојатно се должи на модовите на $\nu_2(\text{AsO}_4)$.

Клучни зборови: магнезиум рубидиум арсенат хексахидрат; магнезиум талиум арсенат хексахидрат; инфрацрвени спектри; рамански спектри

1. INTRODUCTION

Magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (often referred to by its mineralogical name struvite) is a well-known biomineral. Its major biological importance is related to its presence in human urinary sediments and vesical and renal calculi [1, 2]. Besides this, struvite presents a problem in sewage and wastewater treatment. Recovery of phosphorus from waste streams as struvite and recycling these nutrients into agriculture as a fertilizer appears to be a promising potential application [3–6]. More recently, Zhou et al. demonstrated that struvite-type/struvite-related phosphates are promising materials for non-linear optical (NLO) applications [7]. For instance $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$ exhibited the strongest second harmonic generation (SHG) response among the reported UV NLO phosphates related to the presence of isolated and aligned PO_4 groups in the structure of the hexahydrate salt [7].

With this contribution we continue the study of the vibrational spectra of arsenate crystal hydrates with the general formula $\text{M}^1\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{M}^1 = \text{NH}_4, \text{K}, \text{Rb}, \text{Tl}$) having struvite-type or closely related structures which have been a subject of our research in the last fifteen years [8–13]. Here, we have focused on rubidium and thallium representatives, $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ that are very little known. To the best of our knowledge, besides the determination of their crystal structure [14] no other data about the title compounds were reported so far. The aim of the present paper is to report and interpret the infrared and Raman spectra of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ and to give insights on the spectra-structure correlations.

The crystal structures of the title compounds have been determined from single crystal X-ray diffraction at room temperature [14]. They belong to the struvite-type family and crystallize in the orthorhombic system, space group $Pmn2_1$, with $Z =$

2. The crystal lattice of both isostructural compounds is built up from slightly distorted $[\text{Mg}(\text{OH}_2)_6]$ octahedra, AsO_4 tetrahedra and $[\text{M}^1\text{O}_{10}]$ polyhedra ($\text{M}^1, \text{Mg}^{2+}$ and As^{5+} lie on sites with C_s symmetry) which are connected by an extensive network of hydrogen bonds. In the unit cell there are four crystallographically different water molecules of crystallization, two of which have C_s symmetry, while the other two have C_1 symmetry. This results in the formation of seven different hydrogen bonds, six of them between the water molecules and the O atoms of the orthoarsenate groups, while the seventh one is between two water molecules, OW1 and OW2 following the notation given in ref. [14]. The former type of hydrogen bonds can be described as medium to strong ranging from 260.8 to 267.5 pm and 261.7 to 268.1 pm in the Rb and Tl compound, respectively. The latter type is the weakest hydrogen bond present in the crystal lattices with a distance of 313.9 pm in the rubidium compound, accordingly 308.2 pm in the thallium one. It should be mentioned that the hydrogen bond distances in the titled arsenates are very similar to these in $\text{MgKAsO}_4 \cdot 6\text{H}_2\text{O}$ determined at room temperature [9, 15]. Herein, we report the preparation of polycrystalline powders of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$, their deuterated analogues and the subsequent spectroscopic analyses.

2. EXPERIMENTAL

In the literature there are no reports on the synthesis of polycrystalline powders of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$. In this regard, we have designed a precipitation procedure which is similar for the two arsenate salts. The first stage includes mixing of a solution of sodium hydrogenarsenate (10 cm^3 with $c = 0.1\text{ mol/dm}^3$) with a solution of rubidium chloride or thallium nitrate (in both cases 10 cm^3 with $c = 0.2\text{ mol/dm}^3$). Then,

with continuous stirring, solutions of magnesium sulfate (10 cm^3 with $c = 0.25 \text{ mol/dm}^3$) and sodium hydroxide (10 cm^3 with $c = 0.1 \text{ mol/dm}^3$) were successively added. The synthesis was carried out at room temperature. It is interesting to note that in the case of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ synthesis, the precipitation process started with the addition of MgSO_4 solution, while for the $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ synthesis, the precipitation occurred only after the addition of NaOH solution. The beakers containing the respective precipitate and mother liquor were sealed with parafilm and were left in a refrigerator at 5°C . After 5 days of aging the precipitates they were filtered and washed carefully with a small volume of water and a mixture of water/ethanol/acetone (a volume ratio of 1:3:1). The synthesized compounds were dried on the Büchner funnel in an air flow and then at room temperature for 2 hours.

The deuterated analogues were prepared in an analogous procedure as the protiated compounds using H_2O - D_2O mixtures of appropriate composition instead of H_2O .

The infrared spectra of the protiated and deuterated forms of the studied compounds were obtained using the Perkin-Elmer System 2000 infrared interferometer in the $4000\text{--}200 \text{ cm}^{-1}$ region with a resolution of 2 cm^{-1} . Both pressed KBr disks and Nujol mulls at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) were used with 32 spectra being accumulated and averaged. Significant changes were not observed in the spectra recorded in the two matrices: KBr and Nujol mull. LNT spectra were recorded using a low-temperature cell Graseby Specac P/N 21525 with KBr windows. Far infrared spectra were obtained using Nujol and polyethylene pellets.

Raman spectra were recorded at room temperature using a micro-Raman spectrometer LabRam 300 (Horiba Jobin-Yvon). This instrument was equipped with two lasers: He-Ne laser operating at 633 nm (6 mW power on sample) and a double frequency Nd:YAG laser at 532 nm (5 mW power at sample). A microscope Olympus MPlanN with magnification of 50 and 100 was also used. The spectra were recorded with a resolution of 2 cm^{-1} and acquisition times between 10 and 40 s, with 15–30 scans. The GRAMS ANALYST 2000 software package was used for spectra acquisition [16] and GRAMS 32 [17] for spectra management.

X-ray diffractograms of the powder samples of the investigated compounds were recorded and analyzed to confirm the identity of the synthesized products. A Rigaku Ultima IV powder X-ray diffractometer ($\text{CuK}\alpha$ radiation) was used for the X-

ray powder diffraction (XRPD) measurements. Each sample was manually dispersed over a silicon sample plate and the data were collected at room temperature on a D/tex detector in the 2θ range from 5 to 80° (scan rate $2^\circ/\text{min}$). $\text{CuK}\alpha$ radiation was obtained from a generator set at 40 kV and a current of 40 mA . The XRPD patterns (Fig. 1) are typical for the orthorhombic struvite-type arsenate compounds [9]. In addition, the experimental XRPD pattern of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ matches all peaks in the reference pattern (PDF-044-0453).

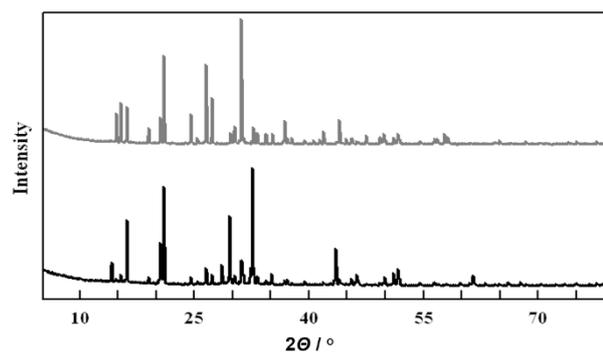


Fig. 1. Scattered intensities as a function of the diffraction angle in $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ (lower curve) and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ (upper curve), (offset spectra are presented). Intensities in the above figure are in arbitrary units ($\text{Intensity} / \text{a. u.}$)

3. RESULTS AND DISCUSSION

The infrared spectra of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT and at boiling liquid nitrogen temperature (LNT) are given in Figures 2 and 3, and their Raman spectra recorded at RT are presented in Figure 4. The assignment of the IR and Raman bands to specific vibrational modes in the spectra of the two salts is given in Tables 1 and 2. As one would expect, the vibrational spectra of the studied two compounds recorded at RT and LNT are very similar due to their isotypism. In addition, they are very similar to the vibrational spectra of $\text{MgKAsO}_4 \cdot 6\text{H}_2\text{O}$ previously reported by our research group [9]. It should be mentioned here that $\text{MgKAsO}_4 \cdot 6\text{H}_2\text{O}$ undergoes a reversible phase transition at 263 K with a transformation from orthorhombic ($Pmn2_1$) to monoclinic ($P112_1$) crystal system [15]. However, our spectroscopic data [9] revealed that this polymorphous transition does not significantly affect the appearance of the LNT IR spectra of the potassium analogue, which are still very much alike the ones obtained for $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$. The identical conclusion has been deduced for the spectra of the other related com-

pounds with formula $M^I M^{II} X O_4 \cdot 6H_2O$ ($M^I = NH_4, K, Rb, Cs, Tl$; $M^{II} = Mg, Co, Ni$; $X = P, As$) no matter if they crystallize in the orthorhombic, hexagonal, cubic or monoclinic system and/or correspondingly they have four, two or one crystallographically different water molecules of crystallization in their structure [8, 9, 13, 18-25]. The only

difference that is evident in these spectra is in the region of the HOH librations and is dependent on the number of the crystallographically different water molecules of crystallization that exist in the structure and the type of the anion (phosphate or arsenate).

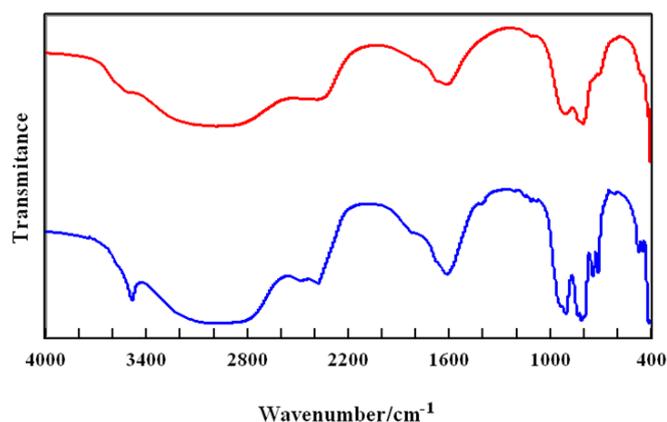


Fig. 2. Infrared spectra of MgRbAsO₄·6H₂O recorded at LNT (lower curve) and at RT (upper curve) (offset spectra are presented).

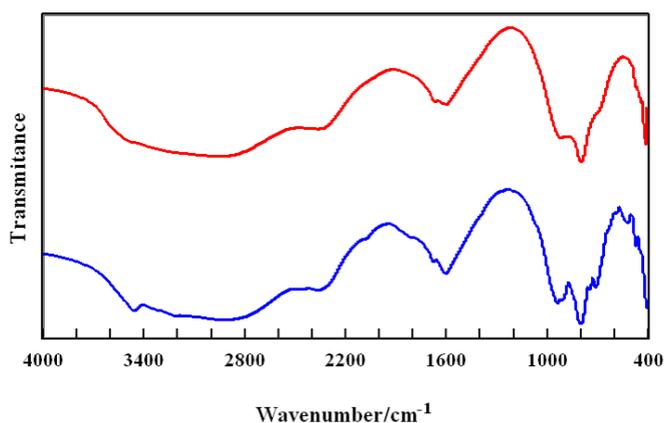


Fig. 3. Infrared spectra of MgTlAsO₄·6H₂O recorded at LNT (lower curve) and at RT (upper curve) (offset spectra are presented).

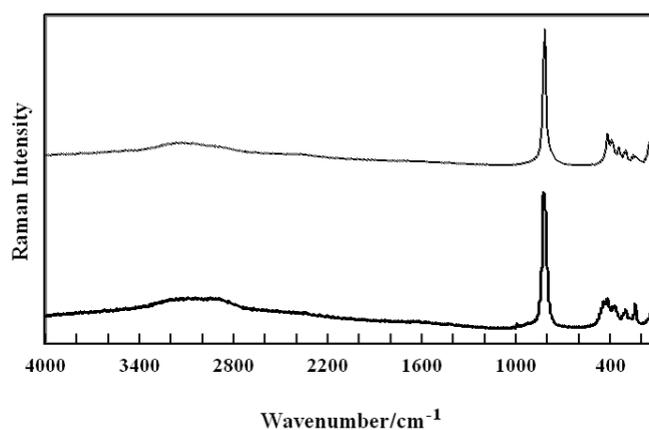


Fig. 4. Raman spectra of MgRbAsO₄·6H₂O (lower curve) and MgTlAsO₄·6H₂O (upper curve) recorded at RT (offset spectra are presented).

Table 1

Assignments of the vibrational bands in the IR and Raman spectra of $MgRbAsO_4 \cdot 6H_2O$ with their estimated intensities ^{a)}

0 % D		about 95 % D				Assignments
IR spectra		Raman spectra	IR spectra		Raman spectra	
RT	LNT	RT	RT	LNT	RT	
3800–2100 vs, br	3800–2000 vs, br	3500–2200 w, br				Related to v(HOH)
			2700–1550 vs, br	2700–1550 vs, br	2600–2000 w, br	Related to v(DOD)
2000–1350 m, br	2000–1350 m, br	1900–1350 vw, br				Related to δ (HOH)
			1350–1000 m, br	1350–1000 m, br	Around 1200 vw	Related to δ (DOD)
	930 s					L(H ₂ O)
900 s	905 s					L(H ₂ O)
828 s	830 s					L(H ₂ O)
735 w	740 m					L(H ₂ O)
704 w	710 m					L(H ₂ O)
		816 vs			824 vs	ν_1 (AsO ₄)
810 vs	810 vs		815 s	820 s		ν_3 (AsO ₄)
				680 s		L(D ₂ O)
				645 m		L(D ₂ O)
				590 m		L(D ₂ O)
				570 m		L(D ₂ O)
				548 m		L(D ₂ O)
				519 m		L(D ₂ O)
470 vw	472 w		460 vw	465 w		related to: v(Mg–O)
442 vw	445 w	436 w	436 vw	435 w		and/or ν_4 (AsO ₄)
	405 m	413 w		401 m	403 vw	ν_2 (AsO ₄)
	362 vw	370 vw		355 vw	370 vw	v(Mg–O)
	303 m	298 vw		293 m	288 vw	v(Mg–O)
	230 m	234 vw		225 m	223 vw	v(Mg–O)
	210 m			205 m		v(Mg–O)

^{a)} Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad, v: stretching, δ : bending, L: libration

Table 2

Assignments of the vibrational bands in the IR and Raman spectra of $MgTlAsO_4 \cdot 6H_2O$ with their estimated intensities ^{a)}

0 % D		About 95 % D				Assignments
IR spectra		Raman spectra	IR spectra		Raman spectra	
RT	LNT	RT	RT	LNT	RT	
3800–2100 vs, br	3800–2000 vs, br	3500–2200 w, br				Related to $\nu(HOH)$
			2700–1550 vs, br	2700–1550 vs, br	2600–2000 w, br	Related to $\nu(DOD)$
2000–1350 m, br	2000–1350 m, br	1900–1350 vw, br				related to $\delta(HOH)$
			1350–1000 m, br	1350–1000 m, br	Around 1200 vw	Related to $\delta(DOD)$
	930 s					L(H_2O)
900 s	905 s					L(H_2O)
	830 m, sh					L(H_2O)
735 w	740 m					L(H_2O)
690 w	700 m					L(H_2O)
		814 vs			821 vs	$\nu_1(AsO_4)$
795 vs	795 vs		805 s	805 s		$\nu_3(AsO_4)$
				675 s		L(D_2O)
				645 m		L(D_2O)
				580 m		L(D_2O)
				555 m		L(D_2O)
				510 m		L(D_2O)
470 vw	470 w		460 vw	458 w		Related to:
440 vw	440 w	430 w	435 vw	435 w		$\nu(Mg-O)$ and/or $\nu_4(AsO_4)$
	405 m	413 w		402 m	403 vw	$\nu_2(AsO_4)$
	383 m	380 vw		375 m	373 vw	$\nu(Mg-O)$
	304 m	335 vw		293 m	330 vw	$\nu(Mg-O)$
	285 w	296 vw		273 w	283 vw	$\nu(Mg-O)$
	223 m	248 vw		219 m	240 vw	$\nu(Mg-O)$

^{a)} Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad, ν : stretching, δ : bending, L: libration

3.1. Internal vibrations of water molecules

The available data is in agreement with the existence of four types of crystallographically different water molecules of crystallization in the crystal structures of the studied compounds [14].

The group theory considerations, previously reported for the orthorhombic struvite-type compounds [8, 9, 18–22, 24], imply that due to the existence of a static field three IR and three Raman active bands are expected from each type of water molecule. Furthermore, taking into account the correlation field, the number of the bands could be significantly increased.

A closer look in the stretching HOH region in the RT and LNT spectra of the titled compounds

(Figs. 2–4) and the spectra of the compounds with formula $M^I M^{II} X O_4 \cdot 6H_2O$ ($M^I = NH_4, K, Rb, Cs, Tl$; $M^{II} = Mg, Co, Ni$; $X = P, As$), no matter the crystal system [8, 9, 13, 18–25], in the region between 3800 cm^{-1} and 2200 cm^{-1} in the IR spectra and between 3500 cm^{-1} and 2200 cm^{-1} in the Raman spectra, one wide and asymmetric band with many shoulders is observed that is more intensive in the IR spectra and is sensitive to deuteration (Figs. 2–4). This is clearly a result of overlapping of several bands resulting in such a wide and asymmetric band. All of these bands are due to stretching vibrations of water molecules and/or are related to them. The position and the width of this asymmetric band infer that medium to strong hydrogen bonds exist in

the structure of the studied compounds which is consistent with the structural data. On the other hand, the sharp band with lower intensity at higher frequency (in general higher than 3450 cm^{-1}), suggests the existence of weaker hydrogen bonds in the systems, which is again in accordance with the structural data. Deuteration also affects these bands shifting them to lower frequencies (Fig. 5).

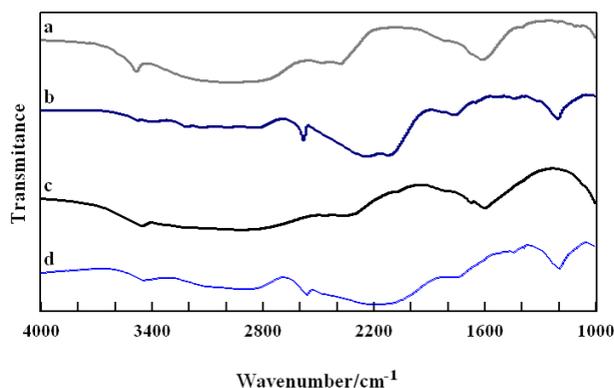


Fig. 5. Infrared spectra recorded at LNT of: $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ (a) and its almost completely deuterated analogue (b); $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ (c) and its almost completely deuterated analogue (d); in the region of the OH/OD stretching vibrations and HOH/DOD bending vibrations (offset spectra are presented.)

The spectral picture of both investigated compounds is similar in the bending HOH region from around 2000 cm^{-1} to 1350 cm^{-1} (Figs. 2–5). Namely, in the LNT IR spectra of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ there are submaxima with lower intensities appearing at around 1810 cm^{-1} , 1670 cm^{-1} , as well as more intensive ones at around 1600 cm^{-1} . The bands in this region are temperature sensitive i.e. the frequency of some of them increases and of some of them decreases with lowering temperature. It should be mentioned here that in the spectra of the cubic form of $\text{MgCsAsO}_4 \cdot 6\text{H}_2\text{O}$ [13], the lowest frequency band in this region is observed at 1520 cm^{-1} which is a frequency lower than the one of the bending HOH vibration of gaseous water (1595 cm^{-1}). Such bands have been observed in the spectra of the compounds with formula $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{XO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{M}^{\text{I}} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$; $\text{M}^{\text{II}} = \text{Mg}, \text{Co}, \text{Ni}$; $\text{X} = \text{P}, \text{As}$) and they can be explained as due to second order transitions, Fermi type of resonance interactions (resonance interactions of overtones of lower frequency modes with $\delta(\text{HOH})$ vibrations) or to coupling with low frequency lattice modes [8–13]. All these mechanisms are generally physically feasible and none of them (or their combination) should be neglected.

3.2. External vibrations of the water molecules

Comparison of the RT and LNT infrared spectra (Figs. 2 and 3) implies temperature sensitivity of all bands below 1000 cm^{-1} . After a systematic analysis of the RT and LNT spectra of the protiated and partially deuterated forms of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ (Figs. 2 and 6), as well as $\text{H}_2\text{O}/\text{D}_2\text{O}$ isotopic shifts of the bands, we assigned the bands at around 930 cm^{-1} , 900 cm^{-1} , and some of the bands around 830 cm^{-1} , 740 cm^{-1} and 710 cm^{-1} to the librational modes (Table 1). In the spectra of the thallium analogue (Figs. 3 and 7), the corresponding bands are assigned at around 930 cm^{-1} , 900 cm^{-1} , and some of the bands around 830 cm^{-1} , 740 and 700 cm^{-1} (Table 2). Namely, all these bands in the spectra of both compounds are quite temperature sensitive (Figs. 2 and 3) and their intensities systematically decrease in the spectra of the deuterated analogues, when increasing the deuterium content (Figs. 6 and 7). Simultaneously, new bands appear which, in the spectrum of the rubidium analogue with highest deuterium content, have wavenumbers of 680 cm^{-1} , 645 cm^{-1} , around 590 cm^{-1} and 570 cm^{-1} , 548 cm^{-1} and 519 cm^{-1} , and in the spectrum of the thallium analogue the corresponding wavenumbers are 675 cm^{-1} , 645 cm^{-1} , around 580 cm^{-1} , 555 cm^{-1} and 510 cm^{-1} , values that are expected if these new bands are indeed due to D_2O librations.

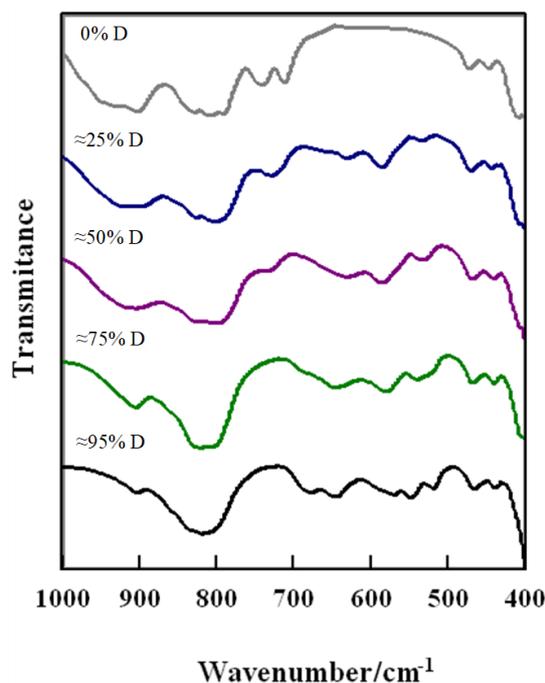


Fig. 6. Infrared spectra of partially and nearly fully deuterated analogues of $\text{MgRbAsO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH external and AsO_4 internal vibrations (the content of deuterium increases from top to bottom, offset spectra are presented.)

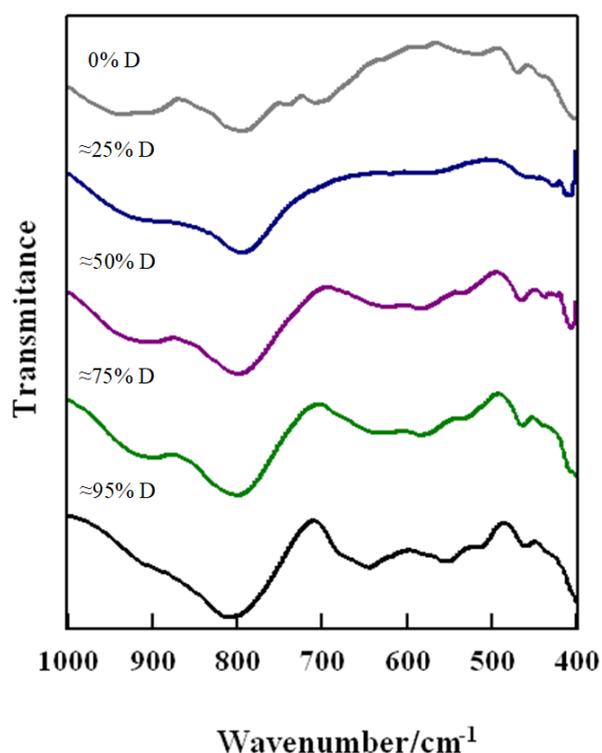


Fig. 7. Infrared spectra of partially and nearly fully deuterated analogues of $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH external and AsO_4 internal vibrations (The content of deuterium increases from top to bottom, offset spectra are presented.)

Furthermore, the high frequencies of some H_2O librational bands arise from the considerable strength of the hydrogen bonds formed by the water molecules [26], which is in accordance with the structural data showing existence of water molecules involved in formation of strong hydrogen bonds [14].

In the Raman spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT, no bands with significant intensity are observed in the region from around 900 cm^{-1} to 500 cm^{-1} that could be attributed to librations of the water molecules (Fig. 4).

3.3. Vibrations of the arsenate ions

Free phosphate ions have tetrahedral symmetry i.e. T_d symmetry. Four normal vibrational modes, ν_1 , ν_2 , ν_3 and ν_4 , exist for this type of groups, vibrations assigned as ν_1 and ν_3 being stretching, and ν_2 and ν_4 bending vibrations. All four modes are Raman active, and ν_3 (antisymmetric stretching vibration) and ν_4 (antisymmetric bending vibration) being IR active.

The group-theory considerations predict that the transformation of the symmetry type from T_d to

C_s gives rise to nine bands in both infrared and Raman spectra corresponding to internal vibrations of the AsO_4^{3-} ion (three components of ν_3 and ν_4 each, two of ν_2 and one of ν_1). Moreover, due to the influence of the correlation field, a total of 15 infrared active and 18 Raman active bands would be expected.

In the region of the ν_3 modes in the LNT IR spectra of the studied compounds, one very intensive and asymmetric band with several shoulders (more prominent in the spectrum of the rubidium analogue) is observed at around 800 cm^{-1} that is very sensitive to temperature and deuterium exchange (Figs. 2, 3, 6 and 7). It was previously discussed that some of these shoulders are due to HOH librations. In the IR spectrum of the analogue with the highest deuterium content this band is less asymmetric with a center at around 820 cm^{-1} for the rubidium compound (Fig. 6) and 805 cm^{-1} for the thallium analogue (Fig. 7). These bands can be with great certainty assigned to the $\nu_3(\text{AsO}_4)$ modes, whereas the less intensive bands to the $\nu_1(\text{AsO}_4)$ vibrations. In this region in the Raman spectra compounds one very intensive band appears at 816 cm^{-1} and 814 cm^{-1} for rubidium and thallium analogue, respectively, that is attributed to the $\nu_1(\text{AsO}_4)$ vibrations. In the spectra of the compounds with the highest deuterium content these bands become narrower and shift to higher wavenumbers, 824 cm^{-1} and 821 cm^{-1} , respectively. This finding suggests that the ν_1 mode is not pure but probably coupled with a libration mode. In line with this hypothesis, as previously mentioned, the bands from the $\nu_1(\text{AsO}_4)$ appear at higher frequencies in the spectra of the analogues with higher deuterium content compared to ones for the protiated analogues.

It should be also noted that in both studied compounds, the $\nu_1(\text{AsO}_4)$ modes appear at higher frequencies than the $\nu_3(\text{AsO}_4)$ vibrations. The same spectral feature has been established in the vibrational spectra of orthorhombic $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgKAsO}_4 \cdot 6\text{H}_2\text{O}$ [8, 9] and the cubic form of $\text{MgCsAsO}_4 \cdot 6\text{H}_2\text{O}$ [13], whereas for $\text{Mg}_2\text{KH}(\text{AsO}_4) \cdot 15\text{H}_2\text{O}$ it was found that both $\nu_1(\text{AsO}_4)$ and $\nu_3(\text{AsO}_4)$ modes have practically the same wavenumbers at around 830 cm^{-1} [11]. This finding is consistent with spectroscopic studies on different arsenate compounds (natural and synthetic) [27–31]. This spectroscopic behavior of ν_1 and ν_3 modes of AsO_4^{3-} is opposite to the commonly observed for other XO_4 tetrahedral groups where the ν_1 wavenumbers are lower than the ν_3 wavenumbers.

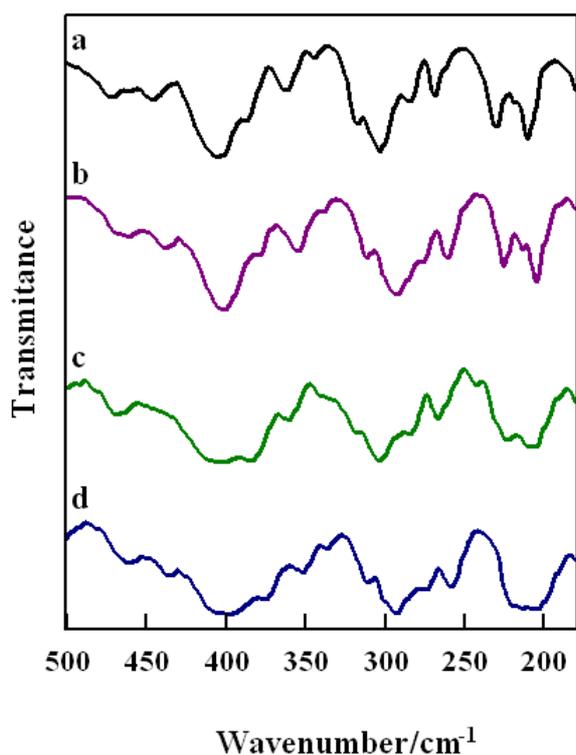


Fig. 8. Far-infrared spectra recorded at LNT of: MgRbAsO₄·6H₂O (a) and its almost completely deuterated analogue (b); MgTlAsO₄·6H₂O (c) and its almost completely deuterated analogue (d); (Offset spectra are presented.)

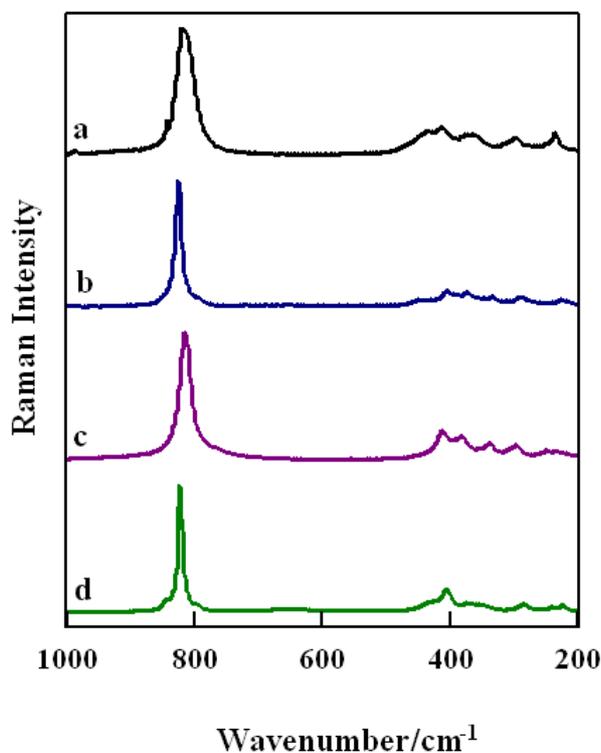


Fig. 9. Raman spectra recorded at RT of: MgRbAsO₄·6H₂O (a) and its almost completely deuterated analogue (b); MgTlAsO₄·6H₂O (c) and its almost completely deuterated analogue (d); in the region of the HOH external and AsO₄ internal vibrations (Offset spectra are presented.)

In the region below 500 cm⁻¹ in the LNT IR spectra of the studied compounds, low intensity bands that are temperature sensitive are observed at 472 cm⁻¹ and 445 cm⁻¹ for the rubidium analogue and at 470 cm⁻¹ and 440 cm⁻¹ for the thallium analogue (Figs. 6 and 7). In the spectra of the partially deuterated analogues (Figs. 6 and 7) these bands are slightly shifted to lower frequencies with increasing the deuterium content. These bands could be assigned as due to stretching Mg–O vibrations and $\nu_4(\text{AsO}_4)$ modes. In the far-infrared (Fig. 8) and Raman spectra (Fig. 9) of both studied compounds many bands are observed in the region between 400 cm⁻¹ and 200 cm⁻¹ most of which being sensitive to deuterium exchange, suggesting that they are not pure but coupled and can be related to $\nu(\text{Mg–Ow})$ modes. On the other hand, the band around 405 cm⁻¹ in the spectra of the protiated compounds most probably originates from the $\nu_2(\text{AsO}_4)$ modes because of its frequency position, intensity and slight sensitivity to deuteration.

4. CONCLUSION

There is a wealth of literature data regarding the analyses of the vibrational spectra of various phosphates, but much less data for the analogous arsenate compounds. The results from this study are a contribution to the understanding of the vibrational spectra of arsenate crystal hydrates with the general formula M^IMgAsO₄·6H₂O (M^I = NH₄, K, Rb, Tl) having struvite-type or closely related structures. Here, the focus was on the very little known rubidium and thallium representatives, MgRbAsO₄·6H₂O and MgTlAsO₄·6H₂O. It has to be pointed out that in their vibrational spectra the $\nu_1(\text{AsO}_4)$ modes appear at higher frequencies than the $\nu_3(\text{AsO}_4)$ modes as in the other previously studied arsenate crystal hydrates. It has also been shown that $\nu_1(\text{AsO}_4)$ and $\nu_3(\text{AsO}_4)$ vibrations are not pure but there is probably coupling between them and/or with some water librational modes. The librational modes appear at quite high frequencies showing existence of strong hydrogen bonds involving water molecules in agreement with the structural data.

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