Crystal structure and vibrational spectra of tetrasodium dimagnesium dihydrogen diphosphate octahydrate $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$

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Abstract

A tetrasodium dimagnesium dihydrogen diphosphate octahydrate $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ was synthesized. It crystallizes in the monoclinic system, space group $P2_1/m$ (no. 11), $Z = 4$, and its unit-cell parameters are: $a = 8.0445(3)$ Å, $b = 11.5244(5)$ Å, $c = 9.0825(4)$ Å, $\beta = 113.1401(2)°$, $V = 774.28(6)$ Å^3. The structure was determined by single-crystal X-ray diffractometry and refined to a R index of 0.0294 ($wR = 0.0727$) for 1878 independent reflections with $I > 2\sigma(I)$. The framework is made by the alternance of layers of MgO_6/NaO_6 octahedra and double tetrahedra PO_4 along b-axis. Such layers are characterized by the presence of strong hydrogen bonds. $(H_2P_2O_7)^{2-}$ anions exhibit bent eclipsed conformation. Besides, the crystal was analyzed by FT–IR and micro-Raman vibrational spectroscopy. No coincidences of the majority of the Raman and infrared spectra bands of $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ confirms a centrosymmetric structure of this material. The vibrational spectra confirm the bent POP configuration in this compound.

1. Introduction

Inorganic acidic diphosphates form a well-known family of compounds which, despite first structure solutions of Corbridge [1] in 1950s, in the last decades have not been frequently topics of systematic structural and vibrational studies. In such structures, there are one or two inorganic cationic species octahedrally coordinated with oxygen atoms, even if large cations may show complex coordination, while diphosphate anion is a double PO_4 tetrahedra with a bridging oxygen atom: P–O–P conformation can be bent or linear, the latter reflecting the presence of a symmetry center. The framework is generally made by infinite chains of cation O_6 octahedra interconnected by double tetrahedra $H_xP_2O_7$ and by strong hydrogen bonds [2].

Among the anhydrous monocationic compounds, we quote systematic work on $Ag_2H_2P_2O_7$ [3], $Cs_2H_2P_2O_7$ [4], and $MnHP_2O_7$ [5], while among the hydrated ones we quote $GdHP_2O_7 \cdot 3H_2O$ [6], $K_2H_2P_2O_7 \cdot 1/2H_2O$ [1], $Na_2H_2P_2O_7 \cdot 6H_2O$ [1,7], $Na_3HP_2O_7 \cdot H_2O$ [8], $Na_3 HP_2O_7 \cdot 9H_2O$ [1], and $Rb_2H_2P_2O_7 \cdot 1/2H_2O$ [9]. For such compounds, the only known vibrational studies corresponds to the $M_3HP_2O_7 \cdot nH_2O$ ($M = K$, Na, Cs; $n = 0$, 1, 9) [10].

Less common is systematic work on dicationic diphosphates, both anhydrous and hydrated. Interesting examples of complex coordinations are present in $Ba_2GaH(P_2O_7)_2$ [11] and $Ca_2KH_3(P_2O_7)_2 \cdot 2H_2O$ [12], where, respectively, Ba atoms are within nine-coordinate cages, and Ca atoms are seven-coordinated, forming distorted pentagonal bipyramid. Recently, Ben Moussa et al. discussed about rare-earth (RE) diphosphates $REHP_2O_7 \cdot 3.5H_2O$ [13], while Assaaoudi et al. [14] discussed on layered dihydrated diphosphate-metallate (II) joined by K^+ cations and hydrogen bonds

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Table 1
Crystal data for $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$

Crystal system	Monoclinic
Space group	$P2_1/m$
a	8.0445(3) Å
b	11.5244(5) Å
c	9.0825(4) Å
β	113.1401(2)°
V	$774.28(6) \times$ Å^3
Z	4
$F(000)$	500
D_c (g cm^{-3})	2.120
Crystal color and shape	Colorless irregular block
Crystal size	$0.35 \times 0.38 \times 0.41$ mm^3
θ range for data collection	4.30–31.96°
μ Mo$K\alpha$ (cm^{-1})	6.79
λ Mo$K\alpha$ (Å)	0.71070
Index ranges	$0 \leqslant h \geqslant 11; 0 \leqslant k \geqslant 17; -13 \leqslant l \geqslant 17$
Reflections number	2116
Refinement method	Full-matrix least-squares on F^2
Refined parameters	144
Observed reflections	1878
R	0.0294
wR	0.0727
GOF	1.096

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$

Atom	x	y	z	U_{iso}[a]
Mg1	0.4689(1)	0.2500	0.73493(9)	0.0144(2)
Na1	0.2439(1)	0.7500	0.9099(1)	0.0273(2)
Na2	−0.0126(1)	0.7500	0.4463(1)	0.0269(2)
P1	0.29602(6)	0.51010(4)	0.64937(5)	0.0155(1)
P2	0.68940(5)	0.49770(3)	0.82906(5)	0.0150(1)
O1	0.2496(2)	0.5616(1)	0.7862(2)	0.0260(3)
O2	0.5044(2)	0.5460(1)	0.6938(2)	0.0239(3)
O3	0.2826(2)	0.3806(1)	0.6433(1)	0.0189(2)
O4	0.1955(2)	0.5775(1)	0.4994(1)	0.0241(3)
O5	0.8303(2)	0.5289(1)	0.7581(2)	0.0229(3)
O6	0.7318(2)	0.5661(1)	0.9797(2)	0.0248(3)
O7	0.6703(2)	0.3697(1)	0.8450(1)	0.0195(2)
O8	0.5641(2)	0.7500	1.0442(2)	0.0201(4)
O9	-0.0398(3)	0.7500	0.7060(3)	0.0288(4)
O10	0.0037(3)	0.7500	0.1977(3)	0.0402(5)
O11	0.5247(3)	0.2500	0.5293(3)	0.0301(5)
H1	0.244(4)	0.518(3)	0.846(3)	0.054(9)
H5	0.817(3)	0.494(2)	0.681(3)	0.035(7)
H8	0.603(3)	0.695(2)	1.021(3)	0.035(7)
H9	−0.089(4)	0.698(2)	0.714(3)	0.057(9)
H10	−0.0604	0.6867	0.1214	0.080
H11	0.566(4)	0.299(2)	0.507(4)	0.07(1)

[a] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[$KM(HP_2O_7) \cdot 2H_2O$ (M = Zn, Mn)]. The present paper is devoted to the elucidation of the crystal structure of a new dicationic acidic diphosphate, $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$: some aspects concerning the synthesis of the compound, the crystal chemistry, and vibrational spectra will also be discussed.

2. Experimental

2.1. Synthesis

$Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ crystals were obtained by mixing two solutions of equimolar quantities of $Na_4P_2O_7$ and $MgCl_2 \cdot 6H_2O$. The pH of the two solutions were controlled with concentrated HCl. The final solution was left at room temperature. Crystals of the title compound appeared in the solution after 5 days.

2.2. X-ray diffraction

The X-ray data for the compound were collected at 293 K on a colorless irregular block crystal of dimension $0.35 \times 0.38 \times 0.41$ mm^3. A Nonius kappa charge coupled device (CCD) area detector diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71070$ Å) was used. 2116 reflections were collected, and omission of intensities with $I \leqslant 2\sigma(I_{obs})$ gave 1878 observed reflections employed for the analysis. For unit-cell refinement 1305 reflections with $1.00° < \theta < 32.03°$ (resolution between 20.40 and 0.67 Å) were used: the crystal is monoclinic, space group $P2_1/m$ ($Z = 4$), $a = 8.0445(3)$ Å, $b = 11.5244(5)$ Å, $c = 9.0825(4)$ Å, $\beta = 113.1401(2)°$, $V = 774.28(6)$ Å^3, $D_c = 2.120$ g cm^{-3}, $F(0 0 0) = 500$. Data were corrected for Lorentz and polarization effects.

The structure was solved through the direct method procedure of SIR97 [15] and refined by a full-matrix least-squares technique, SHELX-L [16]. The final formula of the compound resulted in $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were localized through difference-Fourier map, except H10 which was placed in an idealized position with an assigned isotropic thermal parameter (O10–H10 bond distance is 0.998 Å, U_{iso} is 0.080 Å^2); all hydrogen atoms were refined isotropically. The final cycle of least-squares refinement included 144 parameters (weighting scheme applied: $w^{-1} = [s^2(F_o^2) + (0.0263P)^2 + 0.4230P]$, with $P = [(F_o^2 + 2F_c^2)/3]$).

The final residuals were $R = 0.0294$ and w$R = 0.0727$, while GOF was 1.096. Most significant X-ray data are reported in Table 1, whereas fractional atomic coordinates and equivalent isotropic parameters are reported in Table 2.[1] Molecular drawing was performed by using ORTEP III program [17].
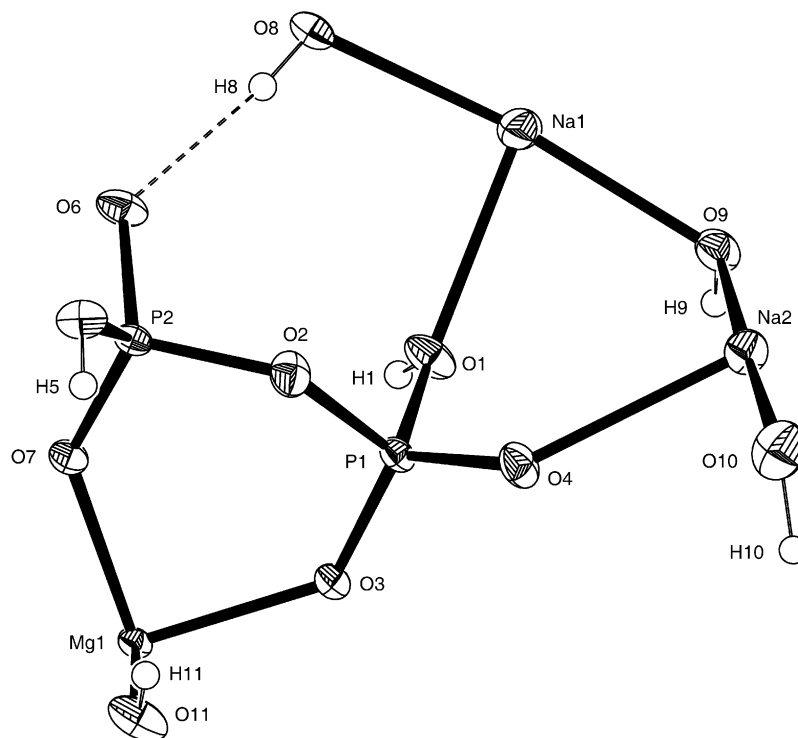
Fig. 1. View of the asymmetric unit of $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ with the atomic numbering scheme.

2.3. Infrared spectrometry

The FT–IR spectrum was recorded on KBr pellet using a ThermoNicolet FT–IR Nexus spectrometer and processed with the Omnic 6.0 software. Pellet was obtained by pressing a mixture of 1 mg of sample and 400 mg of dried KBr (spectrometry grade) under vacuum at 10 tons for 10 min. Instrumental parameters were: spectral range 4000–400 cm^{-1}, 64 scans min^{-1}, resolution 2 cm^{-1}.

2.4. Micro-Raman spectrometry

Micro-Raman measurements were performed in back-scattering geometry at room temperature by using a Dilor XY triple spectrometer equipped with a liquid nitrogen-cooled CCD detector and an adapted Olympus microscope. The spectra were excited with an Ar$^+$ laser (514.5 nm, 3 mW) focused onto a spot of 2 µm in diameter. The scattered light was not analyzed in polarization. The spectral resolution was 0.5 cm^{-1}. The lines of a neon lamp were used for frequency scale calibration. Spectra treatment by suitable software programs was employed to obtain frequencies, line widths and intensities of the Raman bands.

3. Discussion

3.1. Crystal packing

The structure is characterized by seven atoms in special positions: Mg1, Na1, Na2, O8, O9, O10, and O11: each of them has a multiplicity half of the general position. Fig. 1 shows the asymmetric unit with atomic numbering scheme.

The framework is made by the infinite repetition of layers of, respectively, double PO$_4$ tetrahedron and one MgO$_6$ and two NaO$_6$ octahedra (Fig. 2). PO$_4$ tetrahedra share with Mg1O$_6$ octahedra vertices occupied by O7 and O3 oxygen atoms, while with Na1O$_6$ and Na2O$_6$ octahedra share vertices occupied, respectively, by O1 and O3 oxygen atoms; Na2O$_6$ and Mg1O$_6$ octahedra share the O3–O3 edge.

The P–O distances within PO$_4$ tetrahedra of $(H_2P_2O_7)^{2-}$ are comparable to those observed in dihydrogen diphosphate anions from other publications [18–21]. It is possible to distinguish three types of P–O distances: P–O(b) bonds (mean 1.613 Å) corresponding to the bridge oxygen which are the longest ones, P–OH bonds (mean 1.550 Å) involving oxilydril groups, and P–O(ext) corresponding to the external O atoms, which are the shortest ones (mean 1.497 Å). The diphosphate anion show bent eclipsed configuration (see Fig. 1): P1–O2–P2 angle is 131.21(5)°. The average O(b)–P–O(ext) bond angle is 106.25 (5)°.
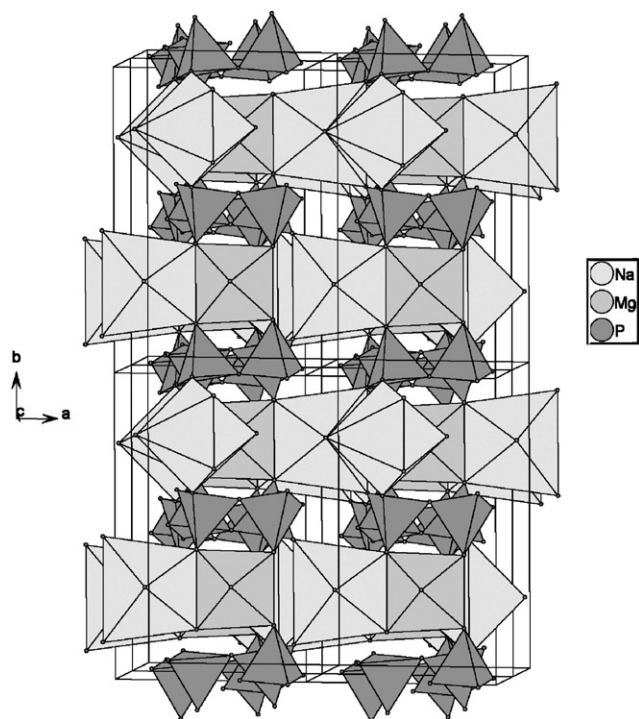
Fig. 2. $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ polyhedra representation ($2 \times 2 \times 2$ cells).

Table 3
Selected bond lengths (Å) and angles (deg) for $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$

Bond lengths			
P1–O3	1.496(1)	Na2–O10	2.313(2)
P1–O4	1.499(1)	Na2–O9	2.453(2)
P1–O1	1.550(1)	Na2–O3[V]	2.501(1)
P1–O2	1.616(1)	Na2–O3[VI]	2.501(1)
		Na2–O4[III]	2.520(1)
		Na2–O4	2.520(1)
P2–O7	1.496(1)	*Angles*	
P2–O6	1.498(1)	P1–O2–P2	131.21(9)
P2–O5	1.550(1)		
P2–O2	1.611(1)		
Mg1–O3[I]	2.056(1)	O1–P1–O2	104.75(8)
Mg1–O3	2.056(1)	O1–P1–O3	112.05(7)
Mg1–O7	2.062(1)	O1–P1–O4	108.42(7)
Mg1–O7[I]	2.062(1)	O2–P1–O3	108.50(7)
Mg1–O11	2.086(2)	O2–P1–O4	103.35(7)
Mg1–O8[II]	2.124(2)	O3–P1–O4	118.55(7)
		O2–P2–O5	102.15(8)
Na1–O9	2.305(2)	O2–P2–O6	108.96(7)
Na1–O8	2.378(2)	O2–P2–O7	108.34(7)
Na1–O1	2.453(1)	O5–P2–O6	108.45(8)
Na1–O1[III]	2.453(1)	O5–P2–O7	112.86(7)
Na1–O7[IV]	2.476(1)	O6–P2–O7	115.23(7)
Na1–O7[II]	2.476(1)		

Symmetry codes: [I]$(x, -y-3/2, z)$; [II]$(1-x, -y-1, 2-z)$; [III]$(x, -y-1/2, z)$; [IV]$(1-x, y+1/2, 2-z)$; [V]$(-x, -1-y, 1-z)$; [VI]$(-x, 1/2+y, 1-z)$.

Mg octahedron is almost regular: Mg–O(basal) distances range from 2.055 up 2.124 Å. The Na1 and Na2 octahedra are slightly distorted. Na1–O distances range from 2.305 up to 2.476 Å, while Na2–O range from 2.313 up to 2.520 Å. The distortion index, calculated as [(Cation–O)$_{max}$–(Cation–O)$_{min}$]/⟨Cation–O⟩ [22], is 0.033 for Mg octahedron, while it increases for Na octahedra, peaking, respectively, 0.070 and 0.084 for Na1 and Na2. This trend is expected on the basis of the shorter Mg^{2+} ionic radius (0.65 Å) with respect to that of Na^+ (0.95 Å): that allows a better packing of the oxygens within the Mg rather than within the Na octahedra. Selected bond lengths and angles are shown in Table 3.

The structure is characterized by the presence of strong hydrogen bonds. The strongest ones are those which concern hydrogen atoms belonging to the $H_2P_2O_7$ group (H1, H5) involved with oxygen atoms of adjacent groups $H_2P_2O_7$, and hydrogen atom H8, bonded to one of Na1 octahedron's oxygen atom, O8, is involved in hydrogen bond with oxygen atom O6 of the P2 tetrahedron. In these cases, the strength of the hydrogen bond is given by the corresponding short O–O (donor–acceptor) distances, which range from 2.542 up to 2.697 Å. Besides, their corresponding H–O (acceptor) distance range from 1.798 up to 1.932 Å.

A fourth hydrogen bond, O9–O5, can be considered less strong in comparison with the above-described

bonds: O–O (donor–acceptor) distance is 2.863 Å, whereas the corresponding H–O(acceptor) distance is 2.146 Å.

The weakest hydrogen bonds are those in which the hydrogen atom is involved in two or three bonds with oxygen acceptor atoms: that is the case of H10 (trifurcated hydrogen bond) and H11 (bifurcated hydrogen bond). Corresponding O–O (donor–acceptor) and H–O (acceptor) range, with respect, from 3.052 up to 3.252 Å and from 2.166 up to 2.913 Å. Bond lengths and angles in the hydrogen-bonding scheme are reported in Table 4.

3.2. Results of vibrational spectroscopy

The Raman and infrared spectra of $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ diphosphate are illustrated in Figs. 3 and 4, respectively. Band assignments for the fundamental modes of this compound are given in Table 5.

In the diphosphate $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$, each $(H_2P_2O_7)^{2-}$ anion possesses three types of distances: P–O(t)$_{terminal}$ due to the PO_2 groups, P–O(b)$_{bridge}$ attributed to the POP bridge and P–OH. Therefore, the band assignments in both Raman and infrared spectra of the title salt are made in terms of the PO_2, POP, P–OH, and O–H vibrations [13,14].

Table 4
Hydrogen bonding scheme for $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$: bond lengths (Å) and angles (deg)

Donor–H	Donor$\cdots$acceptor	H$\cdots$acceptor	Donor–H$\cdots$acceptor
O1–H1	O1$\cdots$O6^{I}	H1$\cdots$O6^{I}	O1–H1$\cdots$O6^{I}
0.757(32)	*2.542(2)*	*1.798(31)*	*167.24(3.14)*
O5–H5	O5$\cdots$O4^{II}	H5$\cdots$O4^{II}	O5–H5$\cdots$O4^{II}
0.777(27)	*2.576(2)*	*1.802(27)*	*174.11(2.61)*
O8–H8	O8$\cdots$O6	H8$\cdots$O6	O8–H8$\cdots$O6
0.769(24)	*2.697(2)*	*1.932(24)*	*172.42(2.32)*
O9–H9	O9$\cdots$O5^{III}	H9$\cdots$O5^{III}	O9–H9$\cdots$O5^{III}
0.733(29)	*2.863(2)*	*2.146(28)*	*166.40(2.84)*
O11–H11	O11$\cdots$O2^{II}	H11$\cdots$O2^{II}	O11–H11$\cdots$O2^{II}
0.721(33)	*3.052(2)*	*2.458(30)*	*140.93(2.85)*
O11–H11	O11$\cdots$O4^{II}	H11$\cdots$O4^{II}	O11–H11$\cdots$O4^{II}
0.721(33)	*3.090(3)*	*2.409(33)*	*158.15(3.14)*
O10–H10	O10$\cdots$O8^{IV}	H10$\cdots$O8^{IV}	O10–H10$\cdots$O8^{IV}
0.998(1)	*3.252(3)*	*2.913(2)*	*100.82(1)*
O10–H10	O10$\cdots$O6^{IV}	H10$\cdots$O6^{IV}	O10–H10Z$\cdots$O6^{IV}
0.998(1)	*3.129(2)*	*2.166(1)*	*161.50(3)*
O10–H10	O10$\cdots$O8^{V}	H10$\cdots$O8^{V}	O10–H10$\cdots$O8^{V}
0.998(1)	*3.252(3)*	*2.913(2)*	*100.82(1)*

Symmetry codes: $^{I}(-x+1, -y-1, -z+2)$; $^{II}(-x+1, -y-1, -z+1)$; $^{III}(x-1, +y, +z)$; $^{IV}(x-1, +y, +z-1)$; $^{V}(x-1, -y-1/2, +z-1)$.
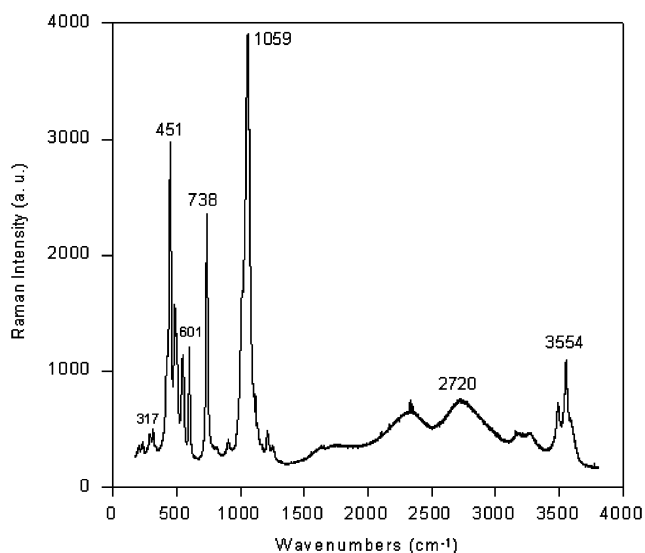

Fig. 3. Raman spectrum of $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$.

Fig. 4. FT–IR spectrum of $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$.

Broadbands in the region of stretching vibrations of water molecules (2500–3800 cm^{-1}) show the presence of a system of hydrogen bonds. The splitting of the stretching vi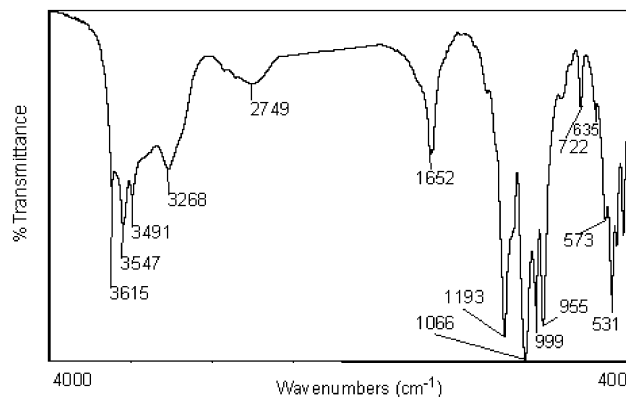brations of H_2O (3800–2500 cm^{-1}) in both Raman and infrared spectra, and of the bending vibrations of water molecules (1652 and 1610 cm^{-1}) in infrared spectrum, and at (1620 and 1752 cm^{-1}) in Raman spectrum show the existence of the non-equivalent positions of water molecules in the crystal lattice [23]. The results of X-ray analysis of the sample $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$ reported in this paper are in good agreement with the spectroscopic data. The frequencies of υOH are localized in both Raman and infrared spectra in the range 2300–3000 cm^{-1}. Bending vibrations δOH are located at 1254 and 1213 cm^{-1} in Raman. The same vibrations are observed at 1268 and 1239 cm^{-1} in infrared spectrum. The liberation of water molecules ρH_2O is located at 601 and 635 cm^{-1} for Raman and infrared spectra, respectively [24].

The terminal stretching modes of $(P_2O_7)^{4-}$ anions usually occur in the region 1250–975 cm^{-1} [25]. The Raman spectrum show eight peaks in the internal mode region, and the most intense band in the Raman spectra at 1059 cm^{-1} is assigned to the symmetric terminal P–O stretching vibration of the PO_2 groups. The infrared spectrum gives five bands, and the asymmetric stretching vibrations of PO_2 groups give the most intense band at 1066 cm^{-1} in the infrared spectrum (Fig. 4).

The bridge vibrations give one Raman peak for the symmetric and antisymmetric mode which are observed at 738 and 906 cm^{-1}, respectively. In the infrared spectrum, only two bands are observed at 722 cm^{-1} (symmetric mode υ_s POP) and 955 cm^{-1} (antisymmetric mode υ_{as} POP). The (weak and broad) bands located at 797 cm^{-1} in Raman, and at 835 and 789 cm^{-1} in infrared spectrum are due to the υP–OH mode [13,14].

The modes lying between 200–320 cm^{-1} in the Raman spectrum can be attributed to the external, torsional, and POP deformation modes. The deformation modes frequency of the POP bridge occurs around 317 cm^{-1} [26], while the rocking and the PO_2 deformation modes are seen in the region 380–600 [13].

Table 5
Band assignments for $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$

Infrared frequency (cm^{-1})	Raman frequency (cm^{-1})	Assignments
3615 m	3569 m(sh)	
3547 m	3554 m	
3491 m	3490 w	υH_2O
	3480 w	
3268 mb	3274 w(sh)	
	3173 w	
	2925 mb	
2749 wb	2720 mb	
	2323 mb	υOH
1652 m	1752 wb	δH_2O
1610 m	1620 wb	
	1254 w	δOH
	1213 w	
1193 s	1168 vw	
1145 m(sh)	1138 vw	
1066 vs	1114 m	$\upsilon_{as}PO_3$ +
999 s	1059 vs	$\upsilon_s PO_3$
	1033 m	
	1009 m	
	981s (sh)	
955 s	906 w	$\upsilon_{as}POP$
835 wb	797 vwb	$\upsilon P-OH$
789 w(sh)		
722 m	738 s	$\upsilon_s POP$
635 w	601 m	ρH_2O
573 m		
531 s	548 m	
502 m	500 m	$\delta PO_3 + \rho PO_3$
460 m	484 m	
425 m	451 s	
	426 m(sh)	
	317 w	δPOP + torsional mode + external modes
	293 w	
	233 vw	
	204 vw	

s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder, υ = stretching, δ = bending, ρ = rocking.

A comparison of the Raman and infrared bands (Table 5) shows that the majority of them are not coincident. This fact confirms a centrosymmetric structure of $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$.

The υ_s POP vibrations is observed only in the Raman spectrum when the bridge is linear. For the bent bridge configuration this vibration appears in both Raman and infrared spectra [27]. In our case, the appearance of υ_s POP (738 and 722 cm^{-1}), respectively, in both Raman and IR spectra indicates a bent configuration in $Na_4Mg_2(H_2P_2O_7)_4 \cdot 8H_2O$, and this is in good agreement with our structural study.

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