

$Synthesis,\ crystal\ structure,\ and\ vibrational\\ spectroscopic\ and\ UV-visible\ studies\ o\ fCs2MnP2O7$

Saida Kaoua, Saida Krimi, Stanislav Péchev, Pierre Gravereau, Jean-Pierre

Chaminade, Michel Couzi, Abdelaziz El Jazouli

▶ To cite this version:

Saida Kaoua, Saida Krimi, Stanislav Péchev, Pierre Gravereau, Jean-Pierre Chaminade, et al.. Synthesis, crystal structure, and vibrational spectroscopic and UV-visible studies of Cs2MnP2O7. Journal of Solid State Chemistry, 2013, 198, pp.379-385. 10.1016/j.jssc.2012.10.016 . hal-00758979

HAL Id: hal-00758979 https://hal.science/hal-00758979

Submitted on 29 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



$Synthesis,\ crystal\ structure,\ and\ vibrational\\ spectroscopic\ and\ UV-visible\ studies\ o\ fCs2MnP2O7$

Saida Kaoua, Saida Krimi, Stanislav Péchev, Pierre Gravereau, Jean-Pierre

Chaminade, Michel Couzi, Abdelaziz El Jazouli

▶ To cite this version:

Saida Kaoua, Saida Krimi, Stanislav Péchev, Pierre Gravereau, Jean-Pierre Chaminade, et al.. Synthesis, crystal structure, and vibrational spectroscopic and UV-visible studies of Cs2MnP2O7. Journal of Solid State Chemistry, Elsevier, 2013, 198, pp.379-385. 10.1016/j.jssc.2012.10.016 . hal-00758979

HAL Id: hal-00758979 https://hal.archives-ouvertes.fr/hal-00758979

Submitted on 29 Jun2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis, crystal structure, and vibrational spectroscopic and UV-visible studies of Cs₂MnP₂O₇

Saida Kaoua^a, Saida Krimi^a, Stanislav Péchev^b, Pierre Gravereau^b, Jean-Pierre Chaminade^b, Michel Couzi^c, Abdelaziz El Jazouli^{d,*}

^a LPCMI, Faculté des Sciences Aïn Chok, UH2C, Casablanca, Morocco

^b CNRS, Université de Bordeaux, ICMCB, 87, Avenue du Dr. A. Schweitzer, Pessac, France

^c CNRS, Université de Bordeaux, ISM, UMR 5255, F-33400 Talence, France

^d LCMS, URAC 17, Faculté des Sciences Ben M'Sik, UH2MC, Casablanca, Morocco

Keywords: Manganese diphosphate Cs₂MnP₂O₇ Crystal structure Infrared Raman UV-Visible

ABSTRACT

A new member of the A_2 MP₂O₇ diphosphate family, Cs₂MnP₂O₇, has been synthesized and structurally characterized. The crystal structure was determined by single crystal X-Ray diffraction. Cs₂MnP₂O₇ crystallizes in the orthorhombic system, space group *Pnma* (#62), with the unit cell parameters a=16.3398(3), b=5.3872(1), c=9.8872(2)Å, Z=4 and V=870.33(3)Å³. The structure parameters were refined to a final $R_1/wR_2=0.0194/0.0441$ for 1650 observed reflections. The 2D framework of Cs₂MnP₂O₇ structure consists of P₂O₇ and MnO₅ units. The corner-shared MnO₅ and P₂O₇ units are alternately arranged along the *b* axis to form [(MnO)P₂O₇]_∞ chains. These chains are interconnected by an oxygen atom to form sheets parallel to the (*b*, *c*) plane. The cesium atoms are located between the sheets in 9- and 10-fold coordinated sites. The infrared and Raman vibrational spectra have been investigated. A factor group analysis leads to the determination of internal modes of (P₂O₇) groups. UV-visible spectrum consists of weak bands, between 340 and 700 nm, assigned to the 0-Mn charge transitions of Mn²⁺ ion, and of a strong band around 250 nm, attributed to the O-Mn charge

1. Introduction

Metal diphosphates have a wide range of applications and can be used as catalysts [1], ionic conductors [2], host laser [3], batteries cathode materials [4,5], pigments [6,7], sunscreens [8]. Among these compounds the diphosphates with the general formula $A_2MP_2O_7$ with A^+ : Alkaline cation (A=Li, Na, K), and M^{2+} : Metal ion (M=Mn, Fe, Co, Ni, Cu, Zn, Pd, Pb) have been extensively investigated in the recent years [9-19]. Their structure depends on the nature of A and M elements. $Li_2MnP_2O_7$ [20] crystallizes in the monoclinic system (space group $P2_1/a$) and is characterized by the presence of Mn₂O₉ units. Li₂CuP₂O₇ [21] crystallizes in the monoclinic system with C_2/c space group and displays tetrahedral coordination of Cu^{II}. K₂MnP₂O₇ [22], K₂CdP₂O₇ [23] and K₂SrP₂O₇ [24] crystallize in the monoclinic system with $P2_1/n$, C2/c and $P2_1/c$ space groups respectively. Na₂CaP₂O₇ [25] crystallizes in the triclinic P-1 space group. K₂CuP₂O₇ [26] crystallizes in the orthorhombic space group *Pbnm*, with square pyramidal coordination for Cu^{II}. The crystals of Na₂CoP₂O₇ [27] exhibit two allotropic forms: triclinic (pink color) and orthorhombic (blue) which display tetrahedral and octahedral coordination of Co^(II) respectively. Similarly, Na₂CuP₂O₇ [28] exists in two allotropic forms (both monoclinic) which differ in coordination geometry of copper (tetrahedral in the high temperature form and square pyramidal in the low temperature form). The structure of Na₂ZnP₂O₇ was described first in the tetragonal space group $P4_2/mnm$ with the small unit cell [9], and in $P4_2/n$ space group with the large unit cell [10]. It is made up of [ZnP₂O₇] layers consisting of corners sharing P₂O₇ groups and isolated ZnO₄ tetrahedra. Na₂MnP₂O₇ [29], which crystallizes in the triclinic space group *P*-1, possesses a new structure type composed of slabs of fused Mn₄P₄O₂₆ cages. NaCsMnP₂O₇ [29] crystallizes in the orthorhombic space group *CmC*₂₁, and its structure resembles that of K₂CuP₂O₇ [26].

We discovered recently two new manganese diphosphates: $Cs_2MnP_2O_7$ and $Rb_2MnP_2O_7 \cdot H_2O$ [30,31]. The present paper is dedicated to $Cs_2MnP_2O_7$. We will describe its synthesis method, its crystal structure solved by using single crystal X-ray diffraction data, and its characterization by infrared, Raman and UV-visible spectroscopies.

2. Experimental

2.1. Synthesis

Crystalline powder of $Cs_2MnP_2O_7$ was prepared from aqueous solutions of $Mn(NO_3)_2 \cdot 4H_2O(I)$, CsCl(II) and $NH_4H_2PO_4(III)$ as

^{*} Corresponding author. Fax: +212 227 04675.

E-mail address: eljazouli_abdelaziz@yahoo.fr (A. El Jazouli).

starting materials. The mixture (precipitate+solution), obtained by slow addition of (III) in (I+II) at room temperature, was dried at about 60 $^{\circ}$ C to remove the liquid. The resulting powder was

Table 1

Crystal data and structure refinement for Cs₂MnP₂O₇.

Formula	Cs ₂ MnP ₂ O ₇
Formula weight	494.70
Crystal size (mm ³)	0.17 × 0.16 × 0.03
Color	Pink
Crystal system	Orthorhombic
Space group	Pnma
Temperature (K)	293(2)
a (Å)	16.3398(3)
b (Å)	5.3872(1)
c (Å)	9.8872(2)
Volume (Å ³)	870.33(3)
Z Calculated density (g/cm ³) Wavelength (Å) Diffractometer Scan method Absorption coefficient (mm ⁻¹) F(000)	4 3.775 0.71073 BRUKER-KAPPA-CCD φ∕ω 10.124 884 2022 20 20
θ range (deg.)	3.23–32.00
Index ranges	$-24 \le h \le 24, -8 \le k \le 8, -14 \le l \le 14$
Reflections collected ($I > 0\sigma(I)$)	35016
Independent reflections ($I > 0\sigma(I)$)	1650 [<i>R</i> (int)=0.0613]
Absorption correction	Gaussian
Max. and min. transmission	0.79 and 0.27
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parametres	1650/0/68
Goodness of fit on F^2	1.127
Final <i>R</i> indices[$I > 2\sigma(I)$]	R_1 =0.0194, wR_2 =0.0441
<i>R</i> indices (all data)	R_1 =0.0231, wR_2 =0.0445
Secondary extinction coefficient	0.0021(2)
Largest diff neak and hole $e^{A^{-3}}$	1.17 (Mn) and -1.02 (Cs2)

then heated progressively from 200 °C up to 700 °C in air atmosphere with intermediate regrindings. $Cs_2MnP_2O_7$ has a pink color.

 $Cs_2MnP_2O_7$ single crystals were obtained by heating the corresponding crystalline powder at 800 °C for 2 h, followed by slow cooling of 10 °C h⁻¹ down to 500 °C and of 20 °C h⁻¹ down to room temperature.

2.2. Single crystal and powder X-ray diffraction

A platelet shaped $Cs_2MnP_2O_7$ pink single crystal of $(0.17 \times 0.16 \times 0.03 \text{ mm}^3)$ has been selected and mounted on glass fiber, for X-ray diffraction analysis. The diffraction data were collected on a Nonius Kappa CCD diffractometer with a graphite monochromator using MoK α radiation. The crystal data and the conditions of data collection are summarized in Table 1.

The purity of the Cs₂MnP₂O₇ powder was checked by X-ray diffraction analysis with a Panalytical X'Pert θ -2 θ (CuK $\alpha_{1,2}$ radiation) diffractometer. The use of "profile matching" option of Fullprof program [32] confirms that all the observed diffracted lines are taken into account by the proposed space group *Pnma*. The observed and calculated XRD patterns together with their difference curves are shown in Fig. 1.

2.3. Vibrational and UV-visible spectroscopies

The infrared spectrum of a mixture of KBr and $Cs_2MnP_2O_7$ (3%) powders was recorded by the diffuse reflection technique using a Bruker IFS Equinox 55 FTIR spectrometer in the range of 1400– 400 cm⁻¹. The Raman spectrum was recorded under the microscope of a Dilor XY Multichannel spectrometer. Excitation was accomplished with 514.5 nm line of argon-ion laser. The diffuse reflectance spectrum was recorded in the range 200–1400 nm at



Fig. 1. Powder X-ray diffraction pattern of Cs₂MnP₂O₇.

room temperature using a Cary 5000 spectrophotometer (VARIAN).

3. Results and discussion

3.1. Structure refinement

The observed extinction conditions for $Cs_2MnP_2O_7$ agree with the *Pnma* space group. The data were corrected for absorption using PLATON program [33]. The structure was solved by direct methods using SHELXS-97 program [34]. The refinement with anisotropic displacement parameters for all atoms converged to R_1 =0.0194 and wR_2 =0.0441 for 68 refined parameters, based on

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² × 10³) for Cs₂MnP₂O₇. U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyckoff site	x	у	Ζ	Site occupancy	U (eq)
Cs(1) Cs(2) Mn P(1) P(2) OB(12) O(12) O(12) O(13) O(22)	4c 4c 4c 4c 4c 4c 8d 4c 8d	4198(1) 1149(1) 1858(1) 2427(1) 4166(1) 3366(2) 2303(1) 1926(2) 4085(1)	1/4 1/4 1/4 1/4 1/4 167(3) 1/4 164(3)	1538(1) 235(1) 3870(1) 7227(1) 7722(1) 6695(2) 8055(2) 5939(3) 8559(2)	1 1 1 1 1 1 1 1 1	211(1) 222(1) 124(1) 124(1) 139(2) 178(5) 200(3) 243(5) 237(4)
O(23)	4c	4877(2)	1/4	6770(3)	1	332(7)

1650 observed reflections. The max and min peaks of the residual electronic density map were in the range between 1.17 and -1.02 eÅ^{-3} . The final atomic coordinates with the equivalent isotropic displacement parameters are presented in Table 2. Selected interatomic distances, bond valences and angles are listed in Table 3. Bond valence sums are calculated using the Brown method [35], $V_i = \sum_j V_{ij}$ and $V_{ij} = \exp[(R_{ij} - d_{ij})/b]$ with b = 0.37, R_{ij} characterizing a cation–anion pair (O^{2–}: 1.790 for Mn²⁺, 2.417 for Cs⁺ and 1.617 for P⁵⁺) and d_{ij} : distance between *i* and *j* atoms. The results are in good agreement with the theoretical values of the expected formal oxidation state of Cs⁺, Mn²⁺ and P⁵⁺ ions (Table 3). Anisotropic displacement parameters for Cs₂MnP₂O₇ are reported in Table 4.

Table 4

Anisotropic displacement parameters (Å² × 10³) for Cs₂MnP₂O₇. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2h k a \times b \times U^{12}]$.

	U^{11}	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cs(1) Cs(2) Mn P(1) P(2) OB12	19(1) 27(1) 16(1) 16(1) 13(1) 20(1)	20(1) 22(1) 9(1) 10(1) 10(1) 20(1)	$25(1) \\18(1) \\13(1) \\12(1) \\19(1) \\14(1)$	0 0 0 0 0 0	1(1) -1(1) -1(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1) -2(1)	0 0 0 0 0
O(12) O(13) O(22) O(23)	19(1) 25(1) 20(1) 19(1)	14(1) 33(1) 14(1) 48(2)	27(1) 15(1) 37(1) 33(2)	7(1) 0 9(1) 0	$0(1) \\ -5(1) \\ -6(1) \\ 11(1)$	0(1) 0 -3(1) 0

Table 3
Bond distances (Å), bond valences (BV) and angles (deg.) for $Cs_2MnP_2O_7$.

	Distance (Å)	BV		Angle (deg.)
$2 \times Cs(1) - O(22)^{a,b}$	3.152(2)	0.137		
$2 \times Cs(1) - O(22)^{c,d}$	3.209(2)	0.119	$2 \times O(12)^{e,d} - Mn - O(22)^{e,t}$	87.5(1)
$2 \times Cs(1)-O(12)^{e,f}$	3.214 (2)	0.116	$2 \times O(12)^{e,f} - Mn - O(22)^{f,e}$	149.4(1)
$2 \times Cs(1) - O(13)^{e,g}$	3.314(2)	0.089	$2 \times O(13) - Mn - O(22)^{e,f}$	100.5(1)
$2 \times Cs(1) - O(23)^{a,h}$	3.512(3)	0.052	$2 \times O(13)$ -Mn-O(12) ^{e,f}	109.9(1)
	⟨3.28⟩	$\sum s = 1.02$	$O(12)^{e}-Mn-O(12)^{f}$	84.2(1)
$Cs(2) - O(23)^{i}$	2.873(3)	0.292	$O(22)^{e}-Mn-O(22)^{f}$	84.8(1)
$2 \times Cs(2) - O(12)^{c,d}$	3.127(2)	0.147		
$2 \times Cs(2) - OB(12)^{e,g}$	3.157(1)	0.135	$O(12)-P(1)-O(12)^{j}$	112.3(1)
$2 \times Cs(2)-O(23)^{e,g}$	3.518(2)	0.051	$2 \times O(12)^{j} - P(1) - O(13)$	112.5(1)
$2 \times Cs(2)-O(22)^{e,f}$	3.606(2)	0.040	$2 \times O(12)^{i} - P(1) - OB(12)$	107.6(1)
	<3.3>	$\sum s = 1.03$	O(13)-P(1)-OB(12)	103.8(1)
Mn-O(13)	2.048(3)	0.498		
$2 \times \text{Mn-O}(22)^{\text{e},\text{f}}$	2.128(2)	0.401	$2 \times O(22)^{i} - P(2) - O(23)$	114.4(1)
$2 \times \text{Mn-O}(12)^{\text{e,f}}$	2.143(2)	0.385	O(22)-P(2)-O(22) ^j	112.6(2)
	(2.12)	$\sum s = 2.07$	O(23)-P(2)-OB(12)	103.1(2)
$2 \times P(1)-O(12)^{j}$	1.513(2)	1.325	$2 \times O(22)^{j} - P(2) - OB(12)$	105.5(1)
P(1)-O(13)	1.514(3)	1.321		
P(1)-OB(12)	1.622(3)	0.987	P(1)-OB(12)-P(2)	123.3(2)
	<1.54>	$\sum s = 4.96$		
P(2)-O(23)	1.495(3)	1.391		
$2 \times P(2) - O(22)^{j}$	1.512(2)	1.328		
P(2) - OB(12)	1.656(3)	0.900		
	<1.54>	$\sum = 4.95$		

Symmetry transformations used to generate equivalent atoms:

^a -x+1, -y, -z+1^b -x+1, y+1/2, -z+1^c x, y, z-1

x - 1/2, y, -2

3.2. Structure description

Cs₂MnP₂O₇ crystallizes in the orthorhombic space group *Pnma*. Fig. 2 shows the projection of its structure on ac plane. It consists of a 2D framework built up from wavy $(MnP_2O_7)^{2-}$ sheets, parallel to the (b, c) plane. The cesium ions are located between these wavy sheets in the inter-layers space, in zigzag positions. These wavy sheets, consists of infinite $[(MnO)P_2O_7]_{\infty}$ chains, running along the *b* axis (Figs. 3 and 4). These chains, formed by P₂O₇ and MnO₅ groups, are connected by the oxygen atom labeled O13. Every MnO₅ polyhedron shares the summits of its base with four PO₄ tetrahedra belonging to two P₂O₇ groups. The fifth summit is linked to another P₂O₇ group by O(13) oxygen.

In the [MnO₅] polyhedron, the four Mn–O distances in the basis of the pyramid $2 \times Mn-O(22)$ and $2 \times Mn-O(12)$ are 2.128(2) and 2.143(2) Å respectively. This is consistent with the sum of the ionic radii (2.13 Å). The fifth one, Mn–O(13): 2.048(3) Å, is significantly shorter as a result of a shift of the Mn atom from the center of the pyramid towards its summit where O(13) is the bridging oxygen between the [(MnO)P₂O₇]_∞ chains (Fig. 3).

The two phosphorus atoms P(1) and P(2) are located in P(1)O₄ and P(2)O₄ tetrahedra, connected by a bridging oxygen OB(12) to form P₂O₇ diphosphate groups which are in eclipsed conformation along P–P axis with P(1)–OB(12)–P(2) angle of 123.2(1)° (Fig. 5). This value is very close to that observed in K₂CuP₂O₇ (120.4°) [26]. The P–O distances (P–O(12), P–O(13), P–O(22), P–O(23)) where every oxygen atom bonds to only one phosphorus are very close to 1.51 Å (Table 3). The P–O bridge distances [P(1)–OB(12):1.622(3) Å; P(2)–OB(12): 1.656(3) Å] where oxygen (O12) bonds to two phosphorus atoms are much larger. All these values are comparable with those observed in other diphosphates [15,22,29].

Fig. 6 presents the different cesium polyhedra in the $Cs_2MnP_2O_7$ diphosphate. Cs^+ ions are found in two different crystallographic sites, Cs(1) is tenfold coordinated, whereas



Fig. 2. Projection of the $Cs_2MnP_2O_7$ structure in (*a*, *c*) plane.



Fig. 3. Connection of MnO_5 and P_2O_7 polyedra forming $[(MnO)P_2O_7]_{\infty}$ chains.



Fig. 4. Connection of $[MnOP_2O_7]_{\infty}$ chains by oxygen O13 forming a sheet parallel to the (b, c) plane.



Fig. 5. P₂O₇ diphosphate group in Cs₂MnP₂O₇.



Fig. 6. Cesium polyhedra in Cs₂MnP₂O₇.

Cs(2) is surrounded by nine oxygen atoms. The Cs–O distances range between 3.152 (3) and 3.512 (3) Å in the $[Cs(1)O_{10}]$ polyhedron and between 2.873 (3) and 3.606(2) Å in the $[Cs(2)O_9]$ polyhedron (Table 3). Since Cs atoms are located between the

 $[MnP_2O_7]$ sheets, it is worth noting that a very short Cs–O bond is observed between Cs(2) and O(23) which is the only "external" oxygen atom of the sheets (Fig. 3).

A comparison with the structure of K₂CuP₂O₇, which belongs to the same space group (#62) but was described according to the Pbnm setting in Ref. [26], shows some similarity in the network built by $[CuP_2O_7]_{\infty}$ chains with K ions situated between sheets. However they differ by the coordination of K (7 and 9- in relation with weaker steric effect), and by the pyramid of Cu^{II} characteristic of Jahn Teller effect with four short distances in the basal plane and the fifth elongated. The Cs₂MnP₂O₇ structure is close to that of NaCsMnP₂O₇ (space group $Cmc2_1$) [29] with nearly equivalent [MnP₂O₇] sheets, nevertheless Cs and Na ions share 12 and five oxygen atoms respectively instead of ten and nine in the title compound. One can notice an oxygen disorder in NaCsMnP₂O₇ where two oxygen positions split with different occupancies. It is not observed in Cs₂MnP₂O₇. Comparison of A_2 MnP₂O₇ (A=Li, Na, K, Rb, Cs) structural features (Table 5) shows that every phosphate adopts a different crystal structure with either layered or 3D [MnP2O7] framework and various Mn coordination [20,22,29-31]. There is a general trend for transition from 3-dimensional to 2-dimensional $[MnO_x]-[P_2O_7]$ framework as the alkaline cation size increases. The alkaline ion coordination rises with the increase of its size.

3.3. Vibrational study of Cs₂MnP₂O₇

The P_2O_7 diphosphate group has the nonlinear angle POP, with $C_{2\nu}$ molecular group. The 21 fundamental vibrations of P_2O_7 groups (3*N*-6) are distributed as follows:

$$\Gamma_{vib}(C_{2v}) = 7A_1 + 4A_2 + 4B_1 + 6B_2$$

Hanuza et al. [36] made a distribution of 21 normal modes of internal vibrations:

- The PO₃ stretching vibrations: $\Gamma_1 = 2A_1 + A_2 + B_1 + 2B_2$
- POP bridge stretching vibrations: $\Gamma_2 = A_1 + B_2$
- The PO₃ deformation vibrations: $\Gamma_3 = 3A_1 + 3A_2 + 3B_1 + 3B_2$
- POP bridge deformation vibrations: $\Gamma_4 = A_1$

 $Cs_2MnP_2O_7$ crystallizes in *Pnma* space group (factor group D_{2h}) with four formula per unit cell. The atoms of phosphorus, manganese and cesium occupy 4*c* sites (site group C_s (σ_{xz})). Table 5 shows the correlations between the molecular group $C_{2\nu}$, the site group C_s and the factor group D_{2h} (using the *Pnma* setting). The irreducible representations corresponding to the internal vibrational modes of the diphosphate groups in the crystal are the following:

 $\Gamma_{v} \text{internal} = 13A_{g} + 8B_{1g} + 13B_{2g} + 8B_{3g} + 8A_{u} + 13B_{1u} + 8B_{2u} + 13B_{3u}$

The A_g , B_{1g} , B_{2g} and B_{3g} modes are Raman active while the B_{1u} , B_{2u} and B_{3u} modes are infrared active. The A_u modes are inactive in both Raman and infrared.

Table 6 Infrared (IR) and Raman (Ra) spectra of $Cs_2MnP_2O_7$ are shown in Fig. 6. Table 7 gives the approximate assignments of the observed peaks Fig. 7. The frequencies of the (P_2O_7) groups are assigned on the basis of the characteristic vibrations of the P–O–P bridge and PO₃ groups [3,36–38]. The assignment of different entities is based on a comparison with structurally related compounds [39] with the following sequence of diphosphate vibrations in the order of decreasing frequency:

$$v_{as}(PO_3) > v_s(PO_3) > v_{as}(P-O-P) > v_s(P-O-P) > \delta(PO_3) > \delta(P-O-P)$$

 v_{as} and v_s refer respectively to asymmetric and symmetric stretching vibrations of P–O bonds in (PO₃) groups or in (P–O–P) bridge; δ refers to deformation modes of O–P–O angles.

The bands and lines observed in the 1200–1022 cm^{-1} region are attributed to the symmetric and the asymmetric stretching vibrations (v_s and v_{as}) of (PO₃) species. The symmetric stretching vibration v_s of (POP) bridges, appearing at around 700 cm⁻¹ as strong Raman lines and weak infrared bands, is characteristic of the P_2O_7 nonlinear group (P-O-P: 123.3(1)°). The asymmetric modes (v_{as} POP) are located around 995–892 cm⁻¹ and give rise to strong infrared bands and weak Raman lines. In the frequency range 600–300 cm⁻¹ the $\delta(PO_3)$ modes are observed, while the δ (POP) bridge modes and the lattice vibrations are situated below 300 cm^{-1} . Hence, the numbers of (IR) and (Ra) peaks, observed in Cs₂MnP₂O₇, are in agreement with those theoretically predicted. Furthermore, the comparison of the Raman and infrared band positions shows that the majority of them are not coincident. This fact is in agreement with the centrosymmetric structure of $Cs_2MnP_2O_7$.

In order to estimate the value of the P–O–P angle α , we used the semi-empirical plot $\Delta = f(\alpha)$ as established by Rulmont et al. [40], where the parameter Δ is defined as [41]

$\Delta = (v_{as} POP - v_s POP) / (v_{as} POP + v_s POP)$

Hence, the estimated value is $\alpha = 127^{\circ}$. The agreement is not so bad with the value of 123.3° as determined by X-ray diffraction (Table 3), given the crude approximations introduced in the model used [42].

3.4. UV-visible study of Cs₂MnP₂O₇

Complexes of transition metals often have absorption bands in the UV-visible region. These bands correspond to the electronic d-d and charge transfer (CT) transitions. Not all these transitions

Table 6 Correlation scheme for the internal modes of $P_2O_7^{4-}$ in Cs₂MnP₂O₇.

Free ion group $C_{2\nu}$	Site group C _s	Factor group D_{2h}
7A ₁ 4A ₂ 4B ₁ 6B ₂	7 <i>A'</i> 4 <i>A''</i> 4 <i>A''</i> 6 <i>A</i> '	$7(A_g + B_{2g} + B_{1u} + B_{3u}) 4(B_{1g} + B_{3g} + A_u + B_{2u}) 4(B_{1g} + B_{3g} + A_u + B_{2u}) 6(A_g + B_{2g} + B_{1u} + B_{3u})$

Table 5

Structural features of A2MnP2O7 (A=Li, Na, K, Rb, Cs) diphosphates.

	Li ₂ MnP ₂ O ₇ [20,31]	Na ₂ MnP ₂ O ₇ [29]	K ₂ MnP ₂ O ₇ [22]	Rb ₂ MnP ₂ O7 [30,31]	Cs ₂ MnP ₂ O ₇ [30,31]
[MnO _x]	MnO ₅ and MnO ₆ MnO ₅ trigonal bipyramid and MnO ₆ octahedron share one edge and form Mn ₂ O ₉ dimer	MnO_6 two MnO_6 octahedra share one edge and form Mn_2O_{10} dimer	MnO ₆ the MnO ₆ octahedra are isolated each from other	MnO_5 the MnO_5 square pyramids are isolated each from other	MnO5 the MnO5 square pyramids are isolated each from other
$[AO_x]$	LiO ₄ LiO ₅	NaO7 NaO8	KO ₈ KO ₉	RbO ₈	CsO ₉ CsO ₁₀
[MnP ₂ O ₇] framework	3D	2D	2D	2D	2D

Table 7	
infrared and Raman band assignments (cm^{-1}) of $Cs_2MnP_2O_7$.	

Cs ₂ MnP ₂ O ₇		Assignments
IR	Raman	
-	1197w	v_{as} (PO ₃) + v_{s} (PO ₃)
1186s	1165vw	
1151m	1154vw	
_	1142vw	
1125m	1129m	
_	1128w	
1097m	1107w	
_	1098w	
_	1081w	
_	1060vw	
1041s	1041w	
10413	1021vs	
_	-	
995m		$P_{\rm P} = O_{\rm P}$
55511	95/1/04	Vas I O I
_	024mm	
_	534VW	
-	-	
85078	858W	
-	-	N D O D
74005	7005	$V_{\rm s}$ P-U-P
=	-	0 (PO ₃)
-	=	
69/W	-	
674VW	-	
661VW	-	
649vw	635W	
623m	598w	
580s	-	
568vs	576w	
-	562m	
526vw	536w	
524vw	521w	
514vw	498vw	
506w	-	
485s	49m	
-	466vw	
465w	-	
457w	-	
441w	-	
429w	428m	
420w	-	
408w	-	
-	364m	
_	327m	δ P-O-P+
_	269w	
_	245w	External modes
	205m	
_	202m	
-	166w	
-	140w	
_	129w	
_	124w	



Fig. 7. Infrared (a) and Raman (b) spectra of Cs₂MnP₂O₇.





we identified in the spectrum the energy level ${}^{4}A_{1g}/{}^{4}E_{g}$, (*G*) because this level is independent of the crystal field parameter, generating a relatively narrow peak. In a second step we identified the other transitions and calculated the crystal field parameter Dq and the Racah parameter B.

Note: vs: very strong, s: strong, m: medium, w- weak, vw: very weak.

have equal intensity. Charge transfer bands are often very strong. The d-d transitions involving final and initial levels with different spins (e.g. Mn^{2+}) are very weak. The d-d transitions could be easily assigned by using Tanabe–Sugano diagrams for octahedral and tetrahedral sites [43]. These diagrams do not exist for square pyramidal sites. However, in a first approximation we could describe the square pyramid as a distorted octahedron with five short bonds and a longest one.

Fig. 8 shows the diffuse reflectance spectrum of $Cs_2MnP_2O_7$. It closely resembles those of $Li_2MnP_2O_7$ [30], $Mn_2P_2O_7$ [44,45] and $Mn_2B_2O_5$ [46]. Mn^{2+} ions occupy octahedral and square pyramidal sites in $Li_2MnP_2O_7$ and only octahedral sites in the two other compounds. The weak peaks observed between 340 and 700 nm in the diffuse reflectance spectrum of $Cs_2MnP_2O_7$ were labeled using the Tanabe–Sugano diagram for the d^5 configuration. First

The absorption peaks observed at 542 (18471), 475 (21077), 416 (24066), 363 (27580) and 348 nm (28768 $\rm cm^{-1})$ are assigned to the d-d transitions in Mn²⁺ from the ground state ${}^{6}A_{1g}$ to the ${}^{4}T_{1g}(G), {}^{4}T_{2g}(G), {}^{4}A_{1g}/{}^{4}E_{g}, (G), {}^{4}T_{2g}(D), {}^{4}E_{g}(D)$ levels, respectively. The band located around 250 nm, more intense than the others, is associated with the $O^{2-}-Mn^{2+}$ charge transfer transition (CT). These O-Mn CT band was also observed in Mn₂P₂O₇ [45], $Mn_{2-x}Mg_{x}P_{2}O_{7}$ [6], LiAlO₂: Mn^{2+} [47] and $Mg_{2}SiO_{4}$: Mn^{2+} [48]. The values of the crystal field and Racah parameters obtained for $Cs_2MnP_2O_7$ (Dq=814 cm⁻¹; B=740 cm⁻¹) are consistent with other manganese (II) compounds: $Li_2MnP_2O_7$ (Dq=904 cm⁻¹, $B = 753 \text{ cm}^{-1}$ [30], $Mg_{1-x}Mn_xP_2O_7$ ($Dq = 804 \text{ cm}^{-1}$, $B = 786 \text{ cm}^{-1}$) [49] and Mn₂B₂O₅ (Dq=939 cm⁻¹, B=751 cm⁻¹) [46]. The Racah parameter *B* is related to the covalence of Mn–O bond. The value of B for Cs₂MnP₂O₇ (753 cm⁻¹) is below the free ion Racah parameter value (920 cm⁻¹) [50,51] indicating a covalent character of Mn–O bond in good agreement with the crystal structure study who showed that Mn–O distances (2.048–2.143 Å) are inferior to the sum of the ionic radii (2.20 Å).

4. Conclusion

A new cesium manganese diphosphate $Cs_2MnP_2O_7$ has been synthesized and structurally characterized. It crystallizes in the orthorhombic system, *Pnma* space group. The framework consists of MnO₅ and P₂O₇ units arranged along *b* axis to form [(MnO)P₂O₇]_∞ chains. These chains are interconnected and form sheets parallel to (*b*, *c*) plane. Cesium atoms are located between the sheets in 9- and 10-fold coordinated sites. The infrared and Raman vibrational study showed a good agreement between the factor group analysis and the spectral assignment. The weak bands observed in the UV–visible spectrum, between 340 and 700 nm, are assigned to the *d*–*d* transitions of Mn²⁺ ion, and the strong band around 250 nm is attributed to the O–Mn charge transfer. Photoluminescence properties of Cs₂MnP₂O₇ and other manganese phosphates are under study and will be published elsewhere.

Acknowledgments

The authors thank Morocco–French financial support (PISC Project-CNRST/CNRS and Volubilis Program-AI no. 10/M/229). A.E.J. thanks Dr. R. Glaum for fruitful discussions.

References

- I. Sádaba, S. Lima, A.A. Valente, M.López Granados, Carbohydr. Res. 346 (2011) 2785.
- [2] H. Fukuoka, H. Matsunaga, S. Yamanaka, Mater. Res. Bull. 38 (2003) 991.
- [3] R. Ternane, M. Ferid, Y. Guyot, M. Trabelsi-Ayadi, G. Boulon, J. Alloys Compd. 464 (2008) 327.
- [4] S. Nishimura, N. Nakamura, R. Natsui, A. Yamada, J. Am. Chem. Soc. 39 (2010) 13596.
- [5] S. Wang, X. Jiang, G. Du, Z. Guo, J. Jang, S.-J. Kim, Mater. Lett. 65 (2011) 3265.
 [6] M. Llusar, A. García, C. Gargori, R. Galindo, J.A. Badenes, G. Monrós, J. Eur.
- Ceram. Soc. 32 (2012) 765. [7] M. Llusar, A. Zielinska, M.A. Tena, J.A. Badenes, G. Monrósa, J. Eur. Ceram. Soc.
- 30 (2010) 1887.
- [8] T. Sato, M. Saito, C. Sato, S. Yin, Funct. Mater. Lett. 2 (2009) 157.
- [9] F. Erragh, A. Boukhari, A. Sadel, E.M. Holt, Acta Crystallogr. C 54 (1998) 1376.
 [10] I. Belharouak, P. Gravereau, C. Parent, J.P. Chaminade, E. Lebraud, G. Le Flem, J. Solid State Chem. 152 (2000) 466.
- [11] A. El Maadi, A. Boukhari, E.M. Holt, J. Chem. Crystallogr. 25 (1995) 531.
- [12] Y. Laligant, Eur. J. Solid State Inorg. Chem. 29 (1992) 83.
- [13] Y. Laligant, Eur. J. Solid State Inorg. Chem. 29 (1992) 239.

- [14] F. Erragh, A. Boukhari, F. Abraham, B. Elouadi, J. Solid State Chem. 152 (2000) 323.
- [15] N. Dridi, A. Boukhari, J.M. Réau, E. Arbib, E.M. Holt, Solid State Ionics 127 (2000) 141.
- [16] F. Sanz, C. Parada, J.M. Rojo, C.R. Valero, R.S. Puche, J. Solid State Chem. 145 (1999) 604.
 [17] N.K. Lokanath, M.A. Sridhar, J.S. Prasad, G.S. Goplakrishna, K.G. Ashamanjari,
- Bull. Mater. Sci. 23 (2000) 175. [18] M. Harchartas, A. Ennaciri, A. Rulmont, B. Gilbert, Spectrochim. Acta Part A 53
- (1997) 245.
 [19] M.J. Mahesh, G.S. Gopalakrishna, K.G. Ashamanjari, Mater. Sci. Semicond.
- [19] M.J. Mahesh, G.S. Gopalakrishna, K.G. Ashamanjari, Mater. Sci. Semicond. Process. 10 (2007) 117.
- [20] L. Adam, A. Guesdon, B. Raveau, J. Solid State Chem. 181 (2008) 3110.
- [21] G.S. Gopalakrishna, M.J. Mahesh, K.G. Ashamanjari, J.S. Prasad, Mater. Res. Bull. 43 (2008) 1171.
- [22] A. El Maadi, A. Boukhari, E.M. Holt, S. Flandrois, C. R. Acad. Sci. Paris 11 (318) (1994) 765.
- [23] R. Faggiani, C. Calvo, Can. J. Chem. 54 (1976) 3319.
- [24] V.K. Trunov, Y.V. Oboznenko, S.P. Sirotinkin, N.B. Tskhelashvili, Neorg. Mater. 27 (1991) 1993.
- [25] J. Bennazha, A. Boukhari, E.M. Holt, Solid State Sci. 1 (1999) 373.
- [26] A. E1Maadi, A. Boukhari, E.M. Holt, J. Alloys Compd. 223 (1995) 13.
- [27] F. Erragh, A. Boukhari, B. Elouadi, E.M. Holt, J. Crystallogr. Spectrosc. Res. 21 (1991) 321.
- [28] F. Erragh, A. Boukhari, F. Abraham, B. Elouadi, J. Solid State Chem. 120 (1995) 23.
- [29] Q. Huang, S.J. Hwu, Inorg. Chem. 37 (1998) 5869.
- [30] S. Kaoua, Thesis, Univesity Hassan II, Casablanca, 2010.
- [31] S. Péchev, S. Kaoua, S. Krimi, P. Gravereau, J.P. Chaminade, A. El Jazouli, Acta Crystallogr. A 67 (2011) C338.
- [32] J. Rodriguez-Carvajal, Fullprof: A Program for Rietveld Refinement and Pattern Matching Analysis, Abstract of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990, p. 127.
- [33] A.L. Spek, J. Appl. Cryst. 36 (2003) 7.
- [34] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany, 1997.
- [35] I.D. Brown, D. Altermatt, Acta Crystallogr. B 41 (1985) 244.
- [36] J. Hanuza, B. Jezowska, K. Lukaszewicz, J. Mol. Struct. 13 (1972) 391.
- [37] M. Serghini Idrissi, L. Rghioui, R. Nejjar, L. Benarafa, M. Saidi Idrissi, A. Lorriaux, F. Wallart, Spectrochim. Acta Part A 60 (2004) 2043.
- [38] M. Ferid, K. Horchani, J. Amami, Mater. Res. Bull. 39 (2004) 1949.
- [39] H. Bih, I. Saadoune, H. Ehrenberg, H. Fuess, J. Solid State Chem. 182 (2009)
- 821.
- [40] A. Rulmont, R. Chay, M. Liégeois-Duyckaerts, P. Tarte, Eur. J. Solid State Inorg. Chem. 28 (1991) 207–219.
- [41] A.N. Lazarev, Vibrational Spectra and Structure of Silicates (English Translation), Consultants Bureau, New York, 1972.
- [42] M. Gabelica-Robert, J. Mol. Struct. 79 (1982) 255.
- [43] Y. Tanabe, S. Sugano, J. Phys. Soc. Jpn. 9 (1954) 766.
- [44] R. Glaum, H. Thauern, A. Schmid, M. Gerk, Z. Anorg. Allg. Chem. 628 (2002) 2800.
- [45] B. Boonchom, R. Baitahe., Mater. Lett. 63 (2009) 2218.
- [46] T. Kawano, H. Morito, H. Yamane., Solid State Sci. 12 (2010) 1419.
- [47] M.G. Brik, H. Teng, H. Lin, S. Zhou, N.M. Avram, J. Alloys Compd. 506 (2010) 4.
- [48] L. Lin, M. Yin, C. Shi, W. Zhang, J. Alloys Compd. 455 (2008) 327.
- [49] T. Kawano, T. Suehiro, T. Sato, H. Yamane, J. Lumin. 130 (2010) 2161.
- [50] B.N. Figgis, Introduction to Ligand Fields, John Willey & Sons, New York, 1976.
- [51] A. Pasternak, Z.B. Goldschmidt, Phys. Rev. A 6 (1972) 55.