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# Synthesis, crystal structure, and vibrational spectroscopic and UV-visible studies of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ 

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## Keywords:

Manganese diphosphate
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Crystal structure
Infrared
Raman
UV-Visible


#### Abstract

A new member of the $A_{2} \mathrm{MP}_{2} \mathrm{O}_{7}$ diphosphate family, $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$, has been synthesized and structurally characterized. The crystal structure was determined by single crystal X-Ray diffraction. $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ crystallizes in the orthorhombic system, space group Pnma (\#62), with the unit cell parameters $a=16.3398(3), b=5.3872(1), c=9.8872(2) \AA, Z=4$ and $V=870.33(3) \AA^{3}$. The structure parameters were refined to a final $R_{1} / w R_{2}=0.0194 / 0.0441$ for 1650 observed reflections. The 2D framework of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ structure consists of $\mathrm{P}_{2} \mathrm{O}_{7}$ and $\mathrm{MnO}_{5}$ units. The corner-shared $\mathrm{MnO}_{5}$ and $\mathrm{P}_{2} \mathrm{O}_{7}$ units are alternately arranged along the $b$ axis to form $\left[(\mathrm{MnO}) \mathrm{P}_{2} \mathrm{O}_{7}\right]_{\infty}$ 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 $\left(\mathrm{P}_{2} \mathrm{O}_{7}\right)$ groups. UV-visible spectrum consists of weak bands, between 340 and 700 nm , assigned to the forbidden $d-d$ transitions of $\mathrm{Mn}^{2+}$ ion, and of a strong band around 250 nm , attributed to the $0-\mathrm{Mn}$ charge transfer.


## 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 $A_{2} \mathrm{MP}_{2} \mathrm{O}_{7}$ with $A^{+}$: Alkaline cation ( $A=\mathrm{Li}, \mathrm{Na}, \mathrm{K}$ ), and $M^{2+}$ : Metal ion ( $M=\mathrm{Mn}, \mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Zn}, \mathrm{Pd}, \mathrm{Pb}$ ) have been extensively investigated in the recent years [9-19]. Their structure depends on the nature of $A$ and $M$ elements. $\mathrm{Li}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ [20] crystallizes in the monoclinic system (space group $P 2_{1} / a$ ) and is characterized by the presence of $\mathrm{Mn}_{2} \mathrm{O}_{9}$ units. $\mathrm{Li}_{2} \mathrm{CuP}_{2} \mathrm{O}_{7}$ [21] crystallizes in the monoclinic system with $\mathrm{C} / \mathrm{c}$ space group and displays tetrahedral coordination of $\mathrm{Cu}^{\mathrm{II}} . \mathrm{K}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ [22], $\mathrm{K}_{2} \mathrm{CdP}_{2} \mathrm{O}_{7}$ [23] and $\mathrm{K}_{2} \mathrm{SrP}_{2} \mathrm{O}_{7}$ [24] crystallize in the monoclinic system with $P 2_{1} / n, C 2 / c$ and $P 2_{1} / c$ space groups respectively. $\mathrm{Na}_{2} \mathrm{CaP}_{2} \mathrm{O}_{7}$ [25] crystallizes in the triclinic $P$-1 space group. $\mathrm{K}_{2} \mathrm{CuP}_{2} \mathrm{O}_{7}$ [26] crystallizes in the orthorhombic space group Pbnm, with square pyramidal coordination for $\mathrm{Cu}^{\mathrm{II}}$. The crystals of $\mathrm{Na}_{2} \mathrm{CoP}_{2} \mathrm{O}_{7}$ [27] exhibit two allotropic forms: triclinic (pink color) and orthorhombic (blue) which display tetrahedral and octahedral coordination of $\mathrm{Co}^{(\mathrm{II})}$ respectively. Similarly, $\mathrm{Na}_{2} \mathrm{CuP}_{2} \mathrm{O}_{7}$ [28] exists in two allotropic forms

[^0](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 $\mathrm{Na}_{2} \mathrm{ZnP}_{2} \mathrm{O}_{7}$ was described first in the tetragonal space group $\mathrm{P}_{2} / \mathrm{mnm}$ with the small unit cell [9], and in $\mathrm{P}_{2} / n$ space group with the large unit cell [10]. It is made up of $\left[\mathrm{ZnP}_{2} \mathrm{O}_{7}\right]$ layers consisting of corners sharing $\mathrm{P}_{2} \mathrm{O}_{7}$ groups and isolated $\mathrm{ZnO}_{4}$ tetrahedra. $\mathrm{Na}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ [29], which crystallizes in the triclinic space group $P-1$, possesses a new structure type composed of slabs of fused $\mathrm{Mn}_{4} \mathrm{P}_{4} \mathrm{O}_{26}$ cages. $\mathrm{NaCsMnP} 2 \mathrm{O}_{7}$ [29] crystallizes in the orthorhombic space group $\mathrm{Cmc}_{1}$, and its structure resembles that of $\mathrm{K}_{2} \mathrm{CuP}_{2} \mathrm{O}_{7}$ [26].

We discovered recently two new manganese diphosphates: $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ and $\mathrm{Rb}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7} \cdot \mathrm{H}_{2} \mathrm{O}$ [30,31]. The present paper is dedicated to $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$. 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 $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ was prepared from aqueous solutions of $\mathrm{Mn}\left(\mathrm{NO}_{3}\right)_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$, $\mathrm{CsCl}(\mathrm{II})$ and $\mathrm{NH}_{4} \mathrm{H}_{2} \mathrm{PO}_{4}(\mathrm{III})$ as
starting materials. The mixture (precipitate+solution), obtained by slow addition of (III) in (I+II) at room temperature, was dried at about $60^{\circ} \mathrm{C}$ to remove the liquid. The resulting powder was

Table 1
Crystal data and structure refinement for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.

| Formula | $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ |
| :--- | :--- |
| Formula weight | 494.70 |
| Crystal size $\left(\mathrm{mm}^{3}\right)$ | $0.17 \times 0.16 \times 0.03$ |
| Color | Pink |
| Crystal system | Orthorhombic |
| Space group | Pnma |
| Temperature (K) | $293(2)$ |
| $a(\AA)$ | $16.3398(3)$ |
| $b(\AA)$ | $5.3872(1)$ |
| $c(\AA)$ | $9.8872(2)$ |
| Volume $\left(\AA^{3}\right)$ | $870.33(3)$ |
| $Z$ | 4 |
| Calculated density $\left(\mathrm{g} / \mathrm{cm}{ }^{3}\right)$ | 3.775 |
| Wavelength $(\AA)$ | 0.71073 |
| Diffractometer | $\mathrm{BRUKER-KAPPA-CCD}$ |
| Scan method | $\phi / \omega$ |
| Absorption coefficient $\left(\mathrm{mm}{ }^{-1}\right)$ | 10.124 |
| $F(000)$ | 884 |
| $\theta$ range (deg.) | $3.23-32.00$ |
| Index ranges | $-24 \leq h \leq 24,-8 \leq k \leq 8,-14 \leq l \leq 14$ |
| Reflections collected $(I>0 \sigma(I))$ | 35016 |
| Independent reflections $(I>0 \sigma(I))$ | $1650[R($ 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 $R$ indices $[I>2 \sigma(I)]$ | $R_{1}=0.0194, w R_{2}=0.0441$ |
| $R$ indices (all data) | $R_{1}=0.0231, w R_{2}=0.0455$ |
| Secondary extinction coefficient | $0.0021(2)$ |
| Largest diff, peak and hole e $\AA-3$ | $1.17(\mathrm{Mn})$ and $-1.02(\mathrm{Cs} 2)$ |

then heated progressively from $200^{\circ} \mathrm{C}$ up to $700^{\circ} \mathrm{C}$ in air atmosphere with intermediate regrindings. $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ has a pink color.
$\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ single crystals were obtained by heating the corresponding crystalline powder at $800^{\circ} \mathrm{C}$ for 2 h , followed by slow cooling of $10^{\circ} \mathrm{C} \mathrm{h}^{-1}$ down to $500^{\circ} \mathrm{C}$ and of $20^{\circ} \mathrm{C} \mathrm{h}^{-1}$ down to room temperature.

### 2.2. Single crystal and powder X-ray diffraction

A platelet shaped $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ pink single crystal of ( $0.17 \times 0.16 \times 0.03 \mathrm{~mm}^{3}$ ) 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 $\alpha$ radiation. The crystal data and the conditions of data collection are summarized in Table 1.

The purity of the $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ powder was checked by X-ray diffraction analysis with a Panalytical X'Pert $\theta-2 \theta\left(\mathrm{CuK} \alpha_{1,2}\right.$ 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 $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ (3\%) powders was recorded by the diffuse reflection technique using a Bruker IFS Equinox 55 FTIR spectrometer in the range of 1400$400 \mathrm{~cm}^{-1}$. 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 $200-1400 \mathrm{~nm}$ at


Fig. 1. Powder X-ray diffraction pattern of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.
room temperature using a Cary 5000 spectrophotometer (VARIAN).

## 3. Results and discussion

### 3.1. Structure refinement

The observed extinction conditions for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ 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 $w R_{2}=0.0441$ for 68 refined parameters, based on

## Table 2

Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7} . U(\mathrm{eq})$ is defined as one-third of the trace of the orthogonalized $U_{i j}$ tensor.

| Atoms | Wyckoff site | $x$ | $y$ | $z$ | Site occupancy | $U(\mathrm{eq})$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{Cs}(1)$ | $4 c$ | $4198(1)$ | $1 / 4$ | $1538(1)$ | 1 | $211(1)$ |
| $\mathrm{Cs}(2)$ | $4 c$ | $1149(1)$ | $1 / 4$ | $235(1)$ | 1 | $222(1)$ |
| Mn | $4 c$ | $1858(1)$ | $1 / 4$ | $3870(1)$ | 1 | $124(1)$ |
| $\mathrm{P}(1)$ | $4 c$ | $2427(1)$ | $1 / 4$ | $7227(1)$ | 1 | $124(1)$ |
| $\mathrm{P}(2)$ | $4 c$ | $4166(1)$ | $1 / 4$ | $7722(1)$ | 1 | $139(2)$ |
| $\mathrm{OB}(12)$ | $4 c$ | $3366(2)$ | $1 / 4$ | $6695(2)$ | 1 | $178(5)$ |
| $\mathrm{O}(12)$ | $8 d$ | $2303(1)$ | $167(3)$ | $8055(2)$ | 1 | $200(3)$ |
| $\mathrm{O}(13)$ | $4 c$ | $1926(2)$ | $1 / 4$ | $5939(3)$ | 1 | $243(5)$ |
| $\mathrm{O}(22)$ | $8 d$ | $4085(1)$ | $164(3)$ | $8559(2)$ | 1 | $237(4)$ |
| $\mathrm{O}(23)$ | $4 c$ | $4877(2)$ | $1 / 4$ | $6770(3)$ | 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 $-1.02 \mathrm{e}^{\circ} \AA^{-3}$. 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], $V_{i}=\sum_{j} V_{i j}$ and $V_{i j}=\exp \left[\left(R_{i j}-d_{i j}\right) / b\right]$ with $b=0.37, R_{i j}$ characterizing a cation-anion pair ( $\mathrm{O}^{2-}: 1.790$ for $\mathrm{Mn}^{2+}, 2.417$ for $\mathrm{Cs}^{+}$and 1.617 for $\mathrm{P}^{5+}$ ) and $d_{i j}$ : distance between $i$ and $j$ atoms. The results are in good agreement with the theoretical values of the expected formal oxidation state of $\mathrm{Cs}^{+}$, $\mathrm{Mn}^{2+}$ and $\mathrm{P}^{5+}$ ions (Table 3). Anisotropic displacement parameters for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ are reported in Table 4.

Table 4
Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h\right.$ $k a \times \mathrm{b} \times \mathrm{U}^{12}$ ].

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

Table 3
Bond distances ( $\AA$ ), bond valences (BV) and angles (deg.) for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.

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

[^1]
### 3.2. Structure description

$\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ 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 $\left(\mathrm{MnP}_{2} \mathrm{O}_{7}\right)^{2-}$ 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 $\left[(\mathrm{MnO}) \mathrm{P}_{2} \mathrm{O}_{7}\right]_{\infty}$ chains, running along the $b$ axis (Figs. 3 and 4). These chains, formed by $\mathrm{P}_{2} \mathrm{O}_{7}$ and $\mathrm{MnO}_{5}$ groups, are connected by the oxygen atom labeled O13. Every $\mathrm{MnO}_{5}$ polyhedron shares the summits of its base with four $\mathrm{PO}_{4}$ tetrahedra belonging to two $\mathrm{P}_{2} \mathrm{O}_{7}$ groups. The fifth summit is linked to another $\mathrm{P}_{2} \mathrm{O}_{7}$ group by $\mathrm{O}(13)$ oxygen.

In the $\left[\mathrm{MnO}_{5}\right]$ polyhedron, the four $\mathrm{Mn}-\mathrm{O}$ distances in the basis of the pyramid $2 \times \mathrm{Mn}-\mathrm{O}(22)$ and $2 \times \mathrm{Mn}-\mathrm{O}(12)$ are $2.128(2)$ and $2.143(2) \AA$ respectively. This is consistent with the sum of the ionic radii ( $2.13 \AA$ ). The fifth one, $\mathrm{Mn}-\mathrm{O}(13)$ : $2.048(3) \AA$, is significantly shorter as a result of a shift of the Mn atom from the center of the pyramid towards its summit where $\mathrm{O}(13)$ is the bridging oxygen between the $\left[(\mathrm{MnO}) \mathrm{P}_{2} \mathrm{O}_{7}\right]_{\infty}$ chains (Fig. 3).

The two phosphorus atoms $\mathrm{P}(1)$ and $\mathrm{P}(2)$ are located in $\mathrm{P}(1) \mathrm{O}_{4}$ and $\mathrm{P}(2) \mathrm{O}_{4}$ tetrahedra, connected by a bridging oxygen $\mathrm{OB}(12)$ to form $\mathrm{P}_{2} \mathrm{O}_{7}$ diphosphate groups which are in eclipsed conformation along $\mathrm{P}-\mathrm{P}$ axis with $\mathrm{P}(1)-\mathrm{OB}(12)-\mathrm{P}(2)$ angle of $123.2(1)^{\circ}$ (Fig. 5). This value is very close to that observed in $\mathrm{K}_{2} \mathrm{CuP}_{2} \mathrm{O}_{7}$ (120.4 ${ }^{\circ}$ ) [26]. The $\mathrm{P}-\mathrm{O}$ distances ( $\mathrm{P}-\mathrm{O}(12), \mathrm{P}-\mathrm{O}(13), \mathrm{P}-\mathrm{O}(22), \mathrm{P}-$ $\mathrm{O}(23)$ ) where every oxygen atom bonds to only one phosphorus are very close to $1.51 \AA$ (Table 3). The P-O bridge distances [ $\mathrm{P}(1)-$ $\mathrm{OB}(12): 1.622(3) \AA ; \mathrm{P}(2)-\mathrm{OB}(12): 1.656(3) \AA$ A where oxygen ( O 12 ) 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 $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ diphosphate. $\mathrm{Cs}^{+}$ions are found in two different crystallographic sites, $\operatorname{Cs}(1)$ is tenfold coordinated, whereas


Fig. 2. Projection of the $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ structure in ( $a, c$ ) plane.


Fig. 3. Connection of $\mathrm{MnO}_{5}$ and $\mathrm{P}_{2} \mathrm{O}_{7}$ polyedra forming $\left[(\mathrm{MnO}) \mathrm{P}_{2} \mathrm{O}_{7}\right]_{\infty}$ chains.


Fig. 4. Connection of $\left[\mathrm{MnOP}_{2} \mathrm{O}_{7}\right]_{\infty}$ chains by oxygen O 13 forming a sheet parallel to the $(b, c)$ plane.


Fig. 5. $\mathrm{P}_{2} \mathrm{O}_{7}$ diphosphate group in $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.


Fig. 6. Cesium polyhedra in $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.
$\mathrm{Cs}(2)$ is surrounded by nine oxygen atoms. The Cs-O distances range between 3.152 (3) and 3.512 (3) $\AA$ in the $\left[\mathrm{Cs}(1) \mathrm{O}_{10}\right.$ ] polyhedron and between 2.873 (3) and $3.606(2) \AA$ in the $\left[\mathrm{Cs}(2) \mathrm{O}_{9}\right]$ polyhedron (Table 3). Since Cs atoms are located between the
[ $\mathrm{MnP}_{2} \mathrm{O}_{7}$ ] sheets, it is worth noting that a very short Cs-O bond is observed between $\mathrm{Cs}(2)$ and $\mathrm{O}(23)$ which is the only "external" oxygen atom of the sheets (Fig. 3).

A comparison with the structure of $\mathrm{K}_{2} \mathrm{CuP}_{2} \mathrm{O}_{7}$, 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 $\left[\mathrm{CuP}_{2} \mathrm{O}_{7}\right]_{\infty}$ 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 $\mathrm{Cu}^{\mathrm{II}}$ characteristic of Jahn Teller effect with four short distances in the basal plane and the fifth elongated. The $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ structure is close to that of $\mathrm{NaCsMnP}_{2} \mathrm{O}_{7}$ (space group $\mathrm{Cmc2}_{1}$ ) [29] with nearly equivalent $\left[\mathrm{MnP}_{2} \mathrm{O}_{7}\right]$ 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 $\mathrm{NaCsMnP} 2 \mathrm{O}_{7}$ where two oxygen positions split with different occupancies. It is not observed in $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$. Comparison of $A_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ ( $A=\mathrm{Li}, \mathrm{Na}, \mathrm{K}, \mathrm{Rb}, \mathrm{Cs}$ ) structural features (Table 5) shows that every phosphate adopts a different crystal structure with either layered or 3D $\left[\mathrm{MnP}_{2} \mathrm{O}_{7}\right]$ framework and various Mn coordination [20,22,29-31]. There is a general trend for transition from 3-dimensional to 2-dimensional $\left[\mathrm{MnO}_{x}\right]-\left[\mathrm{P}_{2} \mathrm{O}_{7}\right]$ framework as the alkaline cation size increases. The alkaline ion coordination rises with the increase of its size.

### 3.3. Vibrational study of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$

The $\mathrm{P}_{2} \mathrm{O}_{7}$ diphosphate group has the nonlinear angle POP, with $\mathrm{C}_{2 v}$ molecular group. The 21 fundamental vibrations of $\mathrm{P}_{2} \mathrm{O}_{7}$ groups ( $3 \mathrm{~N}-6$ ) are distributed as follows:
$\Gamma_{v i b}\left(\mathrm{C}_{2 v}\right)=7 A_{1}+4 A_{2}+4 B_{1}+6 B_{2}$
Hanuza et al. [36] made a distribution of 21 normal modes of internal vibrations:

- The $\mathrm{PO}_{3}$ stretching vibrations: $\Gamma_{1}=2 A_{1}+A_{2}+B_{1}+2 B_{2}$
- POP bridge stretching vibrations: $\Gamma_{2}=A_{1}+B_{2}$
- The $\mathrm{PO}_{3}$ deformation vibrations: $\Gamma_{3}=3 A_{1}+3 A_{2}+3 B_{1}+3 B_{2}$
- POP bridge deformation vibrations: $\Gamma_{4}=A_{1}$
$\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ crystallizes in Pnma space group (factor group $\mathrm{D}_{2 h}$ ) with four formula per unit cell. The atoms of phosphorus, manganese and cesium occupy $4 c$ sites (site group $C_{s}\left(\sigma_{x z}\right)$ ). Table 5 shows the correlations between the molecular group $\mathrm{C}_{2 v}$, the site group $\mathrm{C}_{s}$ and the factor group $\mathrm{D}_{2 h}$ (using the Pnma setting). The irreducible representations corresponding to the internal vibrational modes of the diphosphate groups in the crystal are the following:
$\Gamma_{\nu}$ internal $=13 A_{g}+8 B_{1 g}+13 B_{2 g}+8 B_{3 g}+8 A_{u}+13 B_{1 u}+8 B_{2 u}+13 B_{3 u}$ The $A_{g}, B_{1 g}, B_{2 g}$ and $B_{3 g}$ modes are Raman active while the $B_{1 u}$, $B_{2 u}$ and $B_{3 u}$ modes are infrared active. The $A_{u}$ modes are inactive in both Raman and infrared.

Table 6 Infrared (IR) and Raman (Ra) spectra of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ are shown in Fig. 6. Table 7 gives the approximate assignments of the observed peaks Fig. 7. The frequencies of the $\left(\mathrm{P}_{2} \mathrm{O}_{7}\right)$ groups are assigned on the basis of the characteristic vibrations of the $\mathrm{P}-\mathrm{O}-\mathrm{P}$ bridge and $\mathrm{PO}_{3}$ 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:
$v_{\mathrm{as}}\left(\mathrm{PO}_{3}\right)>v_{\mathrm{s}}\left(\mathrm{PO}_{3}\right)>v_{\mathrm{as}}(\mathrm{P}-\mathrm{O}-\mathrm{P})>v_{\mathrm{s}}(\mathrm{P}-\mathrm{O}-\mathrm{P})>\delta\left(\mathrm{PO}_{3}\right)>\delta(\mathrm{P}-\mathrm{O}-\mathrm{P})$
$v_{a s}$ and $v_{s}$ refer respectively to asymmetric and symmetric stretching vibrations of $\mathrm{P}-\mathrm{O}$ bonds in $\left(\mathrm{PO}_{3}\right)$ groups or in ( $\mathrm{P}-\mathrm{O}-\mathrm{P}$ ) bridge; $\delta$ refers to deformation modes of $\mathrm{O}-\mathrm{P}-\mathrm{O}$ angles.

The bands and lines observed in the $1200-1022 \mathrm{~cm}^{-1}$ region are attributed to the symmetric and the asymmetric stretching vibrations ( $v_{s}$ and $v_{\text {as }}$ ) of $\left(\mathrm{PO}_{3}\right)$ species. The symmetric stretching vibration $v_{s}$ of (POP) bridges, appearing at around $700 \mathrm{~cm}^{-1}$ as strong Raman lines and weak infrared bands, is characteristic of the $\mathrm{P}_{2} \mathrm{O}_{7}$ nonlinear group ( $\mathrm{P}-\mathrm{O}-\mathrm{P}: 123.3(1)^{\circ}$ ). The asymmetric modes ( $v_{a s}$ POP) are located around $995-892 \mathrm{~cm}^{-1}$ and give rise to strong infrared bands and weak Raman lines. In the frequency range $600-300 \mathrm{~cm}^{-1}$ the $\delta\left(\mathrm{PO}_{3}\right)$ modes are observed, while the $\delta($ POP ) bridge modes and the lattice vibrations are situated below $300 \mathrm{~cm}^{-1}$. Hence, the numbers of (IR) and (Ra) peaks, observed in $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$, 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 $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.

In order to estimate the value of the P-O-P angle $\alpha$, we used the semi-empirical plot $\Delta=f(\alpha)$ as established by Rulmont et al. [40], where the parameter $\Delta$ is defined as [41]
$\Delta=\left(v_{a s} \mathrm{POP}-v_{s} \mathrm{POP}\right) /\left(v_{a s} \mathrm{POP}+v_{s} \mathrm{POP}\right)$
Hence, the estimated value is $\alpha=127^{\circ}$. The agreement is not so bad with the value of $123.3^{\circ}$ as determined by X-ray diffraction (Table 3), given the crude approximations introduced in the model used [42].

### 3.4. UV-visible study of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$

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 $\mathrm{P}_{2} \mathrm{O}_{7}^{4-}$ in $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.

| Free ion group $C_{2 v}$ | Site group $C_{s}$ | Factor group $D_{2 h}$ |
| :--- | :--- | :--- |
| $7 A_{1}$ | $7 A^{\prime}$ | $7\left(A_{g}+B_{2 g}+B_{1 u}+B_{3 u}\right)$ |
| $4 A_{2}$ | $4 A^{\prime \prime}$ | $4\left(B_{1 g}+B_{3 g}+A_{u}+B_{2 u}\right)$ |
| $4 B_{1}$ | $4 A^{\prime \prime}$ | $4\left(B_{1 g}+B_{3 g}+A_{u}+B_{2 u}\right)$ |
| $6 B_{2}$ | $6 A^{\prime}$ | $6\left(A_{g}+B_{2 g}+B_{1 u}+B_{3 u}\right)$ |

Table 5
Structural features of $\mathrm{A}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}(A=\mathrm{Li}, \mathrm{Na}, \mathrm{K}, \mathrm{Rb}, \mathrm{Cs})$ diphosphates.

|  | $\mathrm{Li}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}[20,31]$ | $\mathrm{Na}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ [29] | $\mathrm{K}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ [22] | $\mathrm{Rb}_{2} \mathrm{MnP}_{2} \mathrm{O} 7[30,31]$ | $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}[30,31]$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{MnO}_{x}\right]$ | $\mathrm{MnO}_{5}$ and $\mathrm{MnO}_{6}$ | $\mathrm{MnO}_{6}$ | $\mathrm{MnO}_{6}$ | $\mathrm{MnO}_{5}$ the $\mathrm{MnO}_{5}$ square pyramids are isolated each from other | $\mathrm{MnO}_{5}$ <br> the $\mathrm{MnO}_{5}$ square pyramids are isolated each from other |
|  | $\mathrm{MnO}_{5}$ trigonal bipyramid and |  | the $\mathrm{MnO}_{6}$ octahedra are |  |  |
|  | $\mathrm{MnO}_{6}$ octahedron share one edge and form $\mathrm{Mn}_{2} \mathrm{O}_{9}$ dimer | one edge and form $\mathrm{Mn}_{2} \mathrm{O}_{10}$ dimer | isolated each from other |  |  |
| $\left[A O_{x}\right]$ | $\mathrm{LiO}_{4}$ | $\mathrm{NaO}_{7}$ | $\mathrm{KO}_{8}$ | $\mathrm{RbO}_{8}$ | $\mathrm{CsO}_{9}$ |
|  | $\mathrm{LiO}_{5}$ | $\mathrm{NaO}_{8}$ | $\mathrm{KO}_{9}$ |  | $\mathrm{CsO}_{10}$ |
| $\left[\mathrm{MnP}_{2} \mathrm{O}_{7}\right.$ ] <br> framework | 3D | 2D | 2D | 2D | 2D |

Table 7
Infrared and Raman band assignments $\left(\mathrm{cm}^{-1}\right)$ of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.

| $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ |  | Assignments |
| :---: | :---: | :---: |
| IR | Raman |  |
| - | 1197w | $v_{a s}\left(\mathrm{PO}_{3}\right)+v_{s}\left(\mathrm{PO}_{3}\right)$ |
| $1186 \mathrm{~s}$ | 1165vw |  |
| 1151 m | 1154 vw |  |
| - | 1142 vw |  |
| 1125m | 1129 m |  |
| - | 1128w |  |
| 1097m | 1107w |  |
| - | 1098w |  |
| - | 1081w |  |
| - | 1060vw |  |
| 1041s | 1041w |  |
|  | 1021vs |  |
| - | - |  |
| 995m | - | $v_{a s} \mathrm{P}-\mathrm{O}-\mathrm{P}$ |
| - | 954vw |  |
| - | 934vw |  |
| - | - |  |
| 896vs | 898w |  |
| - | - |  |
| 740vs | 700s |  |
| - | - | $\delta\left(\mathrm{PO}_{3}\right)$ |
| - | - |  |
| 697w | - |  |
| 674vw | - |  |
| 661 vw | - |  |
| 649vw | 635w |  |
| 623 m | 598w |  |
| 580s | - |  |
| 568vs | 576w |  |
| - | 562m |  |
| 526vw | 536w |  |
| 524vw | 521w |  |
| $514 \mathrm{vw}$ | 498vw |  |
| 506w | - |  |
| 485s | 49m |  |
| - | 466vw |  |
| 465w | - |  |
| 457w | - |  |
| 441w | - |  |
| 429w | 428m |  |
| 420w | - |  |
| 408w | - |  |
| - | 364 m |  |
| - | 327 m | $\delta \mathrm{P}-\mathrm{O}-\mathrm{P}+$ |
| - | 269w |  |
| - | 245w | External modes |
|  | 205m |  |
| - | 202m |  |
| - | 166w |  |
| - | 140w |  |
| - | 129w |  |
| - | 124w |  |

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. $\mathrm{Mn}^{2+}$ ) 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 $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$. It closely resembles those of $\mathrm{Li}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ [30], $\mathrm{Mn}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ [44,45] and $\mathrm{Mn}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ [46]. $\mathrm{Mn}^{2+}$ ions occupy octahedral and square pyramidal sites in $\mathrm{Li}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ and only octahedral sites in the two other compounds. The weak peaks observed between 340 and 700 nm in the diffuse reflectance spectrum of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ were labeled using the Tanabe-Sugano diagram for the $d^{5}$ configuration. First


Fig. 7. Infrared (a) and Raman (b) spectra of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$.


Fig. 8. Diffuse reflectance spectrum of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$
we identified in the spectrum the energy level ${ }^{4} A_{1 g} /{ }^{4} E_{g}$, (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.

The absorption peaks observed at 542 (18471), 475 (21077), 416 (24066), 363 (27580) and $348 \mathrm{~nm}\left(28768 \mathrm{~cm}^{-1}\right)$ are assigned to the $d-d$ transitions in $\mathrm{Mn}^{2+}$ from the ground state ${ }^{6} A_{1 g}$ to the ${ }^{4} T_{1 g}(G),{ }^{4} T_{2 g}(G),{ }^{4} A_{1 g} /{ }^{4} E_{g}$, (G), ${ }^{4} T_{2 g}(D),{ }^{4} E_{g}(D)$ levels, respectively. The band located around 250 nm , more intense than the others, is associated with the $\mathrm{O}^{2-}-\mathrm{Mn}^{2+}$ charge transfer transition (CT). These $\mathrm{O}-\mathrm{Mn}$ CT band was also observed in $\mathrm{Mn}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ [45], $\mathrm{Mn}_{2-x} \mathrm{Mg}_{x} \mathrm{P}_{2} \mathrm{O}_{7}$ [6], $\mathrm{LiAlO}_{2}: \mathrm{Mn}^{2+}$ [47] and $\mathrm{Mg}_{2} \mathrm{SiO}_{4}: \mathrm{Mn}^{2+}$ [48]. The values of the crystal field and Racah parameters obtained for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}\left(\mathrm{Dq}=814 \mathrm{~cm}^{-1} ; B=740 \mathrm{~cm}^{-1}\right)$ are consistent with other manganese (II) compounds: $\mathrm{Li}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}\left(D q=904 \mathrm{~cm}^{-1}\right.$, $B=753 \mathrm{~cm}^{-1}$ ) [30], $\mathrm{Mg}_{1-x} \mathrm{Mn}_{x} \mathrm{P}_{2} \mathrm{O}_{7}\left(D q=804 \mathrm{~cm}^{-1}, B=786 \mathrm{~cm}^{-1}\right)$ [49] and $\mathrm{Mn}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}\left(D q=939 \mathrm{~cm}^{-1}, B=751 \mathrm{~cm}^{-1}\right)$ [46]. The Racah parameter $B$ is related to the covalence of $\mathrm{Mn}-\mathrm{O}$ bond. The value of $B$ for $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}\left(753 \mathrm{~cm}^{-1}\right)$ is below the free ion Racah parameter value ( $920 \mathrm{~cm}^{-1}$ ) [50,51] indicating a covalent character of $\mathrm{Mn}-\mathrm{O}$ bond in good agreement with the crystal structure study who
showed that Mn-O distances (2.048-2.143 $\AA$ ) are inferior to the sum of the ionic radii $(2.20 \AA)$.

## 4. Conclusion

A new cesium manganese diphosphate $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ has been synthesized and structurally characterized. It crystallizes in the orthorhombic system, Pnma space group. The framework consists of $\mathrm{MnO}_{5}$ and $\mathrm{P}_{2} \mathrm{O}_{7}$ units arranged along $b$ axis to form $\left[(\mathrm{MnO}) \mathrm{P}_{2} \mathrm{O}_{7}\right]_{\infty}$ 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 $\mathrm{Mn}^{2+}$ ion, and the strong band around 250 nm is attributed to the $\mathrm{O}-\mathrm{Mn}$ charge transfer. Photoluminescence properties of $\mathrm{Cs}_{2} \mathrm{MnP}_{2} \mathrm{O}_{7}$ and other manganese phosphates are under study and will be published elsewhere.

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[^1]:    Symmetry transformations used to generate equivalent atoms:
    a $-x+1,-y,-z+1$
    b $-x+1, y+1 / 2,-z+1$
    ${ }^{\text {c }} x, y, z-1$
    ${ }^{\mathrm{d}} x,-y+1 / 2, z-1$
    e $-x+1 / 2,-y, z-1 / 2$
    f $-x+1 / 2, y+1 / 2, z-1 / 2$
    g $-x+1 / 2,-y+1, z-1 / 2$
    h $-x+1,-y+1,-z+1$
    ${ }^{\mathrm{i}} x-1 / 2, y,-z+1 / 2$
    ${ }^{\mathrm{j}} x,-y+1 / 2, z$

