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Journal of Solid State Chemistry 179 (2006) 3724–3730
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

A novel cesium hydroxygallophosphate with a layered structure built up of rutile ribbons: $CsGa_2(OH)_2[(PO_4)H(PO_4)]$

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Received 19 May 2006; received in revised form 1 August 2006; accepted 5 August 2006
Available online 9 August 2006

Abstract

A new cesium gallophosphate, $CsGa_2(OH)_2[(PO_4)H(PO_4)]$, with an original layer structure has been synthesized by hydrothermal route and characterized by single-crystal X-ray diffraction ($R = 0.0344$, $R_w = 0.0319$). Its structure crystallizes in the monoclinic space group $P2_1/a$ with cell parameters $a = 16.079(6)$ Å, $b = 5.9873(12)$ Å, $c = 4.5033(15)$ Å, $\beta = 93.36(4)^\circ$ and $Z = 2$. It consists of $[Ga(OH)PO_4]_\infty$ layers built up of rutile ribbons interconnected through PO_4 tetrahedra. The structure of $CsGa_2(OH)_2[(PO_4)H(PO_4)]$ is closely related to those of $(NH_4)Ga(OH)PO_4$ and $(en)Ga_2(OH)_2(PO_4)_2$ (en = ethylenediamine $[H_3N(CH_2)_2NH_3]^{2+}$). The three structures differ mainly from each other by the relative positions and the spacing of the successive layers, which are governed by different hydrogen bonding modes between $[Ga(OH)PO_4]_\infty$ layers and the interleaved species. The title compound presents strong symmetric hydrogen bonds O—H—O which bridge two PO_4 tetrahedra of two successive layers. As a consequence, the distance between the layers is significantly shorter than in the two other amine compounds.

Keywords: Gallium hydroxyphosphate; Layer structure; Structure determination; Single crystal X-ray diffraction; Hydrothermal synthesis; Hydrogen bonds

1. Introduction

Gallium phosphates represent a great potential for the discovery of open frameworks due to the flexible coordination of gallium, which may be either tetrahedral, octahedral or trigonal bipyramidal. Keeping in mind the analogous behavior of gallium compared to aluminum, many authors investigated the gallium phosphates after the pioneering work of Wilson et al. [1] on aluminophosphates, aiming at the synthesis of microporous oxides. Several gallophosphates templated with organic molecules [2–6] were synthesized. Owing to its rather large size, Cs^+ cation is susceptible to sit in such opened frameworks. The study of cesium gallophosphates is thus of interest to understand this chemistry. Four cesium gallophosphates with a tunnel structure are actually known: the tetrametaphosphate $CsGa(PO_3)_4$ [7], the pentaphosphate $CsGa_2P_5O_{16}$ [8], one form of the triphosphate $CsGaHP_3O_{10}$ [9] and the hydroxyphosphate $Cs_2Ga_6(OH)_2(PO_4)_6 \cdot xH_2O$ [10]. The ability of cesium gallophosphates to form layered structures is exemplified by the triphosphate $Cs_2GaP_3O_{10}$ [11] and three forms of $CsGaHP_3O_{10}$ [12–14], whereas 1D structures were observed for the diphosphate $Cs_2GaH_3(P_2O_7)_2$ [15] and $Cs_2Ga(H_2PO_4)(HPO_4)_2H_3PO_4 \cdot 0.5H_2O$ [16]. We have revisited the Cs–Ga–P–O system using hydrothermal synthesis. We report herein on a new hydroxygallophosphate with a layer structure built up of rutile ribbons interconnected with monophosphate groups. We show that this structure is characterized by extremely short and symmetric hydrogen bonds which reinforce the cohesion between the layers. The structural relationships with the layered phosphates $(NH_4)Ga(OH)PO_4$ [17] and (en)-$Ga_2(OH)_2(PO_4)_2$ (en = ethylenediamine $[H_3N(CH_2)_2NH_3]^{2+}$) [18] are also studied.

2. Chemical synthesis of $CsGa_2(OH)_2[(PO_4)H(PO_4)]$

Synthesis of the title compound was performed hydrothermally in 21 ml Teflon-lined stainless-steel Parr

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doi:10.1016/j.jssc.2006.08.002

autoclaves. Single crystals were obtained by mixing 1 ml of deionized water with CsOH (50%, Alfa Aesar), Ga_2O_3 (0.225 g, Alfa Aesar, 99.9%) and H_3PO_4 (85%, Prolabo Rectapur) in the Cs:Ga:P molar ratio corresponding to 1:2:2. This acidic solution (pH $\approx$ 1) was heated at 473 K for 75 h and then cooled down to room temperature at 10°/h. The resulting product (pH $\approx$ 3) was filtered off, washed with water and dried in air. A white powder containing colorless rod-like crystals was obtained.

Attempts to obtain a monophasic sample for further analysis revealed that bulk synthesis of the product is quite difficult. The metastable character of the phase was obviously evidenced by the presence of numerous secondary cesium-containing phases (at least seven) in experiments performed at the stoechiometric composition. Nevertheless, a sample with only Ga_2O_3 as by-product has been synthesized at the 1:1:1 ratio for Cs:Ga:P.

Attempts to substitute Cs by Rb and Ga by In or Al were not conclusive.

3. Single crystal X-ray diffraction study

Semi-quantitative analyses of colorless crystals extracted from the preparation were performed with an OXFORD 6650 microprobe mounted on a PHILIPS XL30 FEG scanning electron microscope. They revealed the presence of Cs, Ga and P elements in the approximate 21:37:42 percentage in the crystals, in agreement with the cationic composition deduced from the single crystal X-ray diffraction study (20:40:40).

A colorless single crystal with a rod-like shape parallel to ***b*** axis was selected to be studied with a BRUKER-NONIUS Kappa CCD four-circle diffractometer equipped with a two-dimensional CCD detector and using Mo*K*α radiation. The data collection was made at 293 K, using the experimental conditions listed in Table 1. The cell parameters reported were accurately determined from the whole registered frames. Data were reduced and corrected for Lorentz and polarization effects with the EvalCCD package [19]. Structure determination, refinement and corrections for absorption and secondary extinction effects [20] were performed with the JANA2000 program [21].

The observed systematic absences $h0l: h = 2n+1$ and $0k0: k = 2n+1$ correspond to the centrosymmetric space group $P2_1/a$ (no. 14). This non-standard setting has been chosen in order to compare easily the structure obtained with that of $(NH_4)Ga(OH)PO_4$ [17]. The position of non-hydrogen atoms (except Cs(2)) was first determined using the heavy atom method and successive difference Fourier synthesis and Fourier synthesis. The refinement of the atomic coordinates and the anisotropic atomic displacement parameters of all these atoms led to reliability factors $R = 0.0464$ and $R_w = 0.0502$, with Cs(1) site fully occupied. However, a strong residue of $4.46\,e^-/Å^3$ appeared on the Fourier difference at approximate coordinates (0.5, 0.25, 0), as well as three residues of ca. $2.3\,e^-/Å^3$ around Ga(1). These residues strongly decreased while refining the occupancy of Cs(1) site to 0.935(3), whereas the residue at (0.5, 0.25, 0) still remained at $3.82\,e^-/Å^3$ with $R = 0.0423$ and $R_w = 0.0462$. Better reliability factors $R = 0.0353$ and $R_w = 0.0339$ were obtained after the introduction of Cs(2) at (0.5, 0.25, 0), the sum of occupancies of the two cesium sites being restrained to one atom per unit cell. This restrained refinement led to site occupancies of 0.9252(18) and 0.0374(9) for Cs(1) and Cs(2), respectively (Table 2). Note that the occupancy of the Cs(1) site remains close to its initial value. A free refinement of the two occupancies would have led to values of 0.937(2) for Cs(1) and 0.044(2) for Cs(2), corresponding to 1.025(6) cesium per unit cell. This result justifies the restriction imposed on the occupancies of the Cs sites.

Table 1
Summary of crystal data, intensity measurements and structure refinement parameters for $CsGa_2(OH)_2[(PO_4)H(PO_4)]$

(1) *Crystal data*	
Crystal dimensions	0.150 × 0.036 × 0.015 mm
Space group	$P2_1/a$
Cell parameters	$a = 16.079(6)$ Å
	$b = 5.9873(12)$ Å
	$c = 4.5033(15)$ Å
	$\beta = 93.36(4)°$
Volume	432.8(2) $Å^3$
Z	2
Formula weight	497.3 $g\,mol^{-1}$
ρ calc	3.8151 $g \cdot cm^{-3}$
(2) *Intensity measurements*	
λ (Mo*K*α)	0.71069 Å
Scan strategies	φ and ω scans
	0.5°/frame
	150 s/°
	Two iterations
	$Dx = 36$ mm
θ Range for data collection and limiting indices	$5.87° \leqslant \theta \leqslant 39.99°$
	$-28 \leqslant h \leqslant 28$
	$-10 \leqslant k \leqslant 10$
	$-8 \leqslant l \leqslant 2$
R_{int}	0.0687
Measured reflections	5792
Independent reflections	2677
Independant reflections with $I > 3\sigma$	1361
μ (mm^{-1})	10.78
Absorption correction method	Gaussian
Absorption coefficient	$T_{min} = 0.551$, $T_{max} = 0.878$
Secondary extinction method	B-C type 1 Gaussian isotropic
Secondary extinction coefficient	$0.09(2) \times 10^{-4}$
(3) *Structure solution and refinement*	
Parameters refined	84
Reliability factors	$R = 0.0344$, $R_w = 0.0319$
Refinement with	F
Weighting scheme	$w = 1/(\sigma(F)^2 + 1 \times 10^{-4} F^2)$
Δ/σ max	6×10^{-4}

The examination of bond valence sum (BVS) calculations [22] led for the cationic elements (i.e. cesium, gallium and phosphorus) to values close to the theoretical ones (i.e.

1, 3 and 5, respectively). Most of oxygen anions present the expected value of 2, except O(3) and O(4) for which the BVS calculated values are 1.58 and 1.23, respectively, suggesting the presence of at least one hydroxyl group on O(4) atom. The final Fourier difference exhibits residues of ca. 1 $e^-/\text{Å}^3$ among which hydrogen atoms have been located near O(4) and O(3) atoms. Note that H(3) atom sits on a inversion center so that it is shared between two O(3) atoms. This ensures the charge balance of the structure. Positional parameters of H atoms were refined isotropically with atomic displacement parameter fixed at approximately 1.3-fold the equivalent isotropic parameters of the oxygen atoms to which they are bonded [23].

Table 2
Positional parameters, atomic displacement parameters, site occupancy and their estimated standard deviations in $CsGa_2(OH)_2[(PO_4)H(PO_4)]$

Atom	x	y	z	U_{eq} (Å^2)	Site occ.
Cs(1)	0.5	0.5	0	0.02415(11)	0.9252(18)
Cs(2)	0.5016(5)	0.2634(15)	1.003(2)	0.047(3)	0.0374(9)
Ga(1)	0.25277(2)	0.13426(6)	−0.00206(8)	0.00738(9)	1
P(1)	0.35625(5)	−0.11959(13)	0.54469(17)	0.00776(19)	1
O(1)	0.30054(14)	−0.1164(3)	0.2467(5)	0.0106(6)	1
O(2)	0.33996(13)	0.0968(3)	0.7116(5)	0.0103(6)	1
O(3)	0.44718(14)	−0.1403(4)	0.4689(6)	0.0189(7)	1
O(4)	0.31286(13)	0.3882(3)	0.1732(5)	0.0092(6)	1
O(5)	0.33359(13)	−0.3299(3)	0.7147(5)	0.0117(6)	1
H(3)	0.5	0	0.5	0.024	1
H(4)	0.322(2)	0.360(6)	0.382(9)	0.012	1

The two Cs sites occupancies have been restrained to obtain one cesium atom per asymmetric unit of the cell.
Isotropic parameters (fixed values) were used for H atoms. All other atoms were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter U_{eq} defined by $U_{eq} = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a^{*i} a^{*j} \vec{a}_i \vec{a}_j$.

The final atomic coordinates, equivalent isotropic displacement parameters, site occupancies and their estimated standard deviations are listed in Table 2. They correspond to reliability factors $R = 0.0344$ and $R_w = 0.0319$. The distances and angles in the structure are reported in Table 3 and the BVS calculations in Table 4. Further details of the crystal structure investigations (including anisotropic displacement parameters and F_o–F_c lists) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de), on quoting the depositery number CSD-416504.

4. Description of the structure

The projections of the structure of this new gallophosphate along [001] (Fig. 1a) and [0$\bar{1}$0] (Fig. 2a) show that it consists of $GaO_4(OH)_2$ octahedra and PO_4 tetrahedra forming $[Ga(OH)PO_4]_\infty$ layers parallel to (100). In the

Table 3
Selected bond distances (Å) and angles (°) in $CsGa_2(OH)_2[(PO_4)H(PO_4)]$

Ga(1)	O(1)	O(1^{i})	O(2^{ii})	O(4)	O(4^{iii})	O(5^{iv})
O(1)	**1.999(2)**	4.015(3)	2.831(3)	3.047(3)	2.549(3)	2.769(3)
O(1^{i})	177.41(9)	**2.016(2)**	2.853(3)	2.549(3)	2.992(3)	2.794(3)
O(2^{ii})	90.94(9)	91.30(9)	**1.972(2)**	2.768(3)	2.831(3)	3.937(3)
O(4)	101.19(9)	80.10(9)	89.94(9)	**1.944(2)**	3.887(3)	2.765(3)
O(4^{iii})	80.50(9)	98.10(9)	92.56(9)	176.96(9)	**1.945(2)**	2.702(3)
O(5^{iv})	88.63(9)	89.13(9)	179.56(9)	90.05(9)	87.46(9)	**1.964(2)**

P(1)	O(1)	O(2)	O(3)	O(5)
O(1)	**1.569(2)**	2.502(3)	2.511(3)	2.495(3)
O(2)	107.74(12)	**1.528(2)**	2.530(3)	2.557(3)
O(3)	108.43(14)	111.91(13)	**1.526(2)**	2.467(3)
O(5)	107.30(12)	113.52(13)	107.74(13)	**1.529(2)**

Cs(1)–O(3^{v})	3.293(2)	Cs(2)–O(1^{vii})	3.547(9)
Cs(1)–O(3^{vi})	3.167(3)	Cs(2)–O(2^{ii})	3.012(9)
Cs(1)–O(3^{vii})	3.167(3)	Cs(2)–O(2^{viii})	3.522(9)
Cs(1)–O(3^{viii})	3.293(2)	Cs(2)–O(3^{ii})	3.486(9)
Cs(1)–O(4)	3.223(2)	Cs(2)–O(3)	3.349(10)
Cs(1)–O(4^{ix})	3.223(2)	Cs(2)–O(3^{vii})	2.439(10)
Cs(1)–O(5^{v})	3.073(2)	Cs(2)–O(3^{viii})	2.577(10)
Cs(1)–O(5^{viii})	3.073(2)	Cs(2)–O(4)	3.259(9)
		Cs(2)–O(5^{viii})	2.898(9)

			O–H (Å)	O–H—O (°)	H—O (Å)	O—O (Å)
O(4)	H(4)	O(2)	0.96(4)	144(3)	2.17(4)	2.998(3)
O(3)	H(3)	O(3^{viii})	1.197(2)	180	1.197(2)	2.394(3)

Symmetry codes: (i) $1/2-x, 1/2+y, -z$; (ii) $x, y, -1+z$; (iii) $1/2-x, -1/2+y, -z$; (iv) $1/2-x, 1/2+y, 1-z$; (v) $x, 1+y, -1+z$; (vi) $x, 1+y, z$; (vii) $1-x, -y, -z$; (viii) $1-x, -y, 1-z$; (ix) $1-x, 1-y, -z$.

latter (Fig. 3), each gallium octahedron shares two opposite edges with two other octahedra and forms rutile ribbons $[GaO_2(OH)_2]_\infty$ running along ***b***, whereas each PO_4 tetrahedron shares two apices with two successive octahedra of the same ribbon, and a third apex with a second ribbon, its fourth apex being free. As a result, each $GaO_4(OH)_2$ octahedron shares four apices with four PO_4 tetrahedra, its two remaining apices corresponding to hydroxyl groups, with hydrogen atoms in *trans*-positions along the rutile ribbon, as schematized on Fig. 3.

Table 4
Bond valence sum calculations for cesium, gallium, phosphorus and oxygen atoms in $CsGa_2(OH)_2[(PO_4)H(PO_4)]$

	Cs(1)	Cs(2)	Ga(1)	P(1)	
O(1)		0.00	0.48 0.46	1.10	2.05
O(2)		0.02 0.00	0.52	1.23	1.76
O(3)	0.09 0.12 0.12 0.09	0.00 0.01 0.07 0.05		1.23	1.58
O(4)	0.11 0.11	0.01	0.56 0.56		1.23
O(5)	0.16 0.16	0.02	0.53	1.22	1.93
	0.95	0.18	3.12	4.79	

For cesium atoms, the site occupancies have been introduced in the BVS calculation.

One important feature of this structure deals with the fact that the free oxygen apices of the PO_4 tetrahedra belonging to two different layers are separated by short O—O distances of 2.4 Å. The Fourier difference shows that beside the hydroxyl groups belonging to the gallium octahedra, there exists a hydrogen atom shared by these two PO_4 tetrahedra and located at equal distances of their apical corners. It results in strong symmetric hydrogen bonds O—H—O, leading to bond valence of 0.5 for H—O, in agreement with the parameters calculated by Brown and Altermatt [24]. Such symmetric hydrogen bonds shared between two PO_4 tetrahedra and characterized by a short O—O distance of about 2.4 Å have previously been observed in several hydroxyphosphates [9,12–15,25–28 for example]. They reinforce strongly the cohesion between the layers. For this reason, the formula of this phosphate should be written $CsGa_2(OH)_2[(PO_4)H(PO_4)]$.

5. Discussion

The interatomic distances (Table 3) show that the PO_4 tetrahedra are practically regular with P–O distances ranging from 1.528(2) to 1.569(2) Å, the longest distance corresponding to the bond with the triply-bonded O(1) atom. The $GaO_4(OH)_2$ octahedra are slightly distorted, with Ga–O distances ranging from 1.944(2) to 2.016(2) Å. The shortest ones correspond to the bonds with the hydroxyl groups O(4)–H(4). The longest Ga–O distances involve the oxygen atoms connecting rutile ribbons with phosphate groups, and especially O(1). The O(4)–H(4) distance is usual (0.96(4) Å). It forms classic weak hydrogen bonds inside the layer between two rutile ribbons, with O(4)—O(2) distance of about 2.998(3) Å

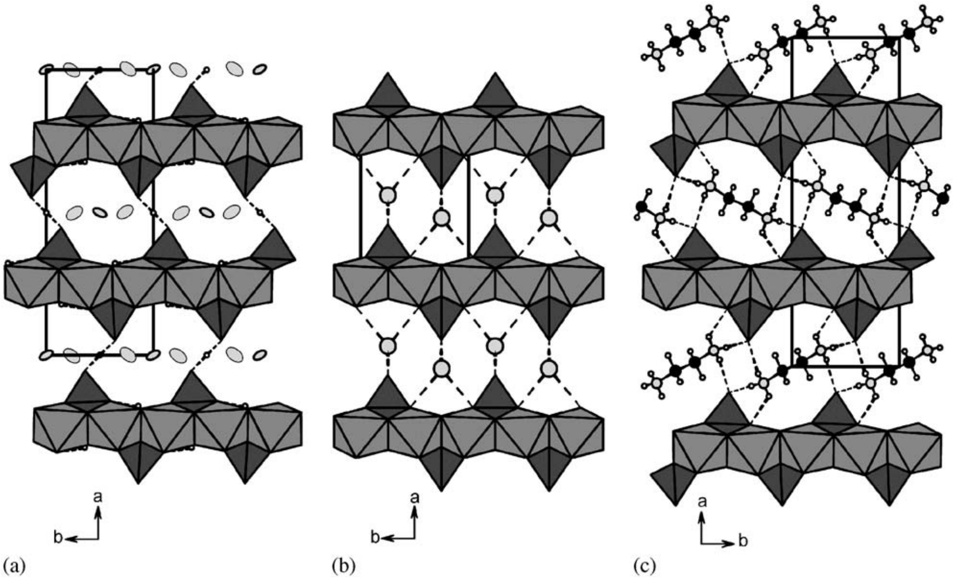

Fig. 1. View at the same scale of $CsGa_2(OH)_2[(PO_4)H(PO_4)]$ (a), $(NH_4)Ga(OH)PO_4$ (b) along [001], and $(en)Ga_2(OH)_2(PO_4)_2$ (c) along $[00\bar{1}]$. PO_4 tetrahedra are colored in dark gray and $Ga(OH)_2O_4$ octahedra in medium gray. Cs(1) and Cs(2) cations are drawn with thick and thin light gray circles, respectively (displacement ellipsoid at 70% probability level). Nitrogen and carbon atoms are drawn isotropically with light gray and black circles, respectively. Small isotropic white circles represent hydrogen atoms. Dashed black lines represent hydrogen bonds.

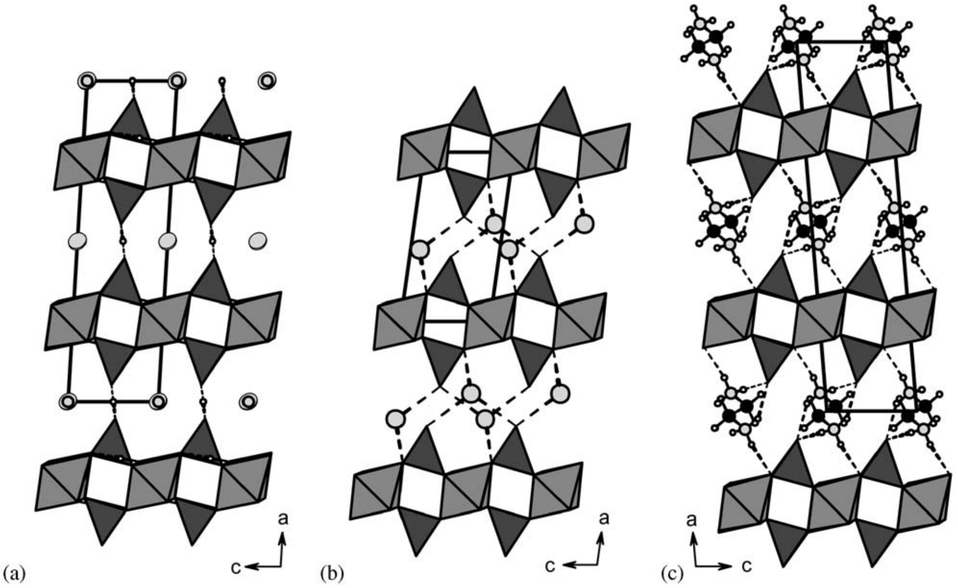

Fig. 2. View at the same scale of $CsGa_2(OH)_2[(PO_4)H(PO_4)]$ **(a),** $(NH_4)Ga(OH)PO_4$ **(b)** along [0$\bar{1}$0], and $(en)Ga_2(OH)_2(PO_4)_2$ **(c)** along [010]. See Fig. 1 for complete legend.

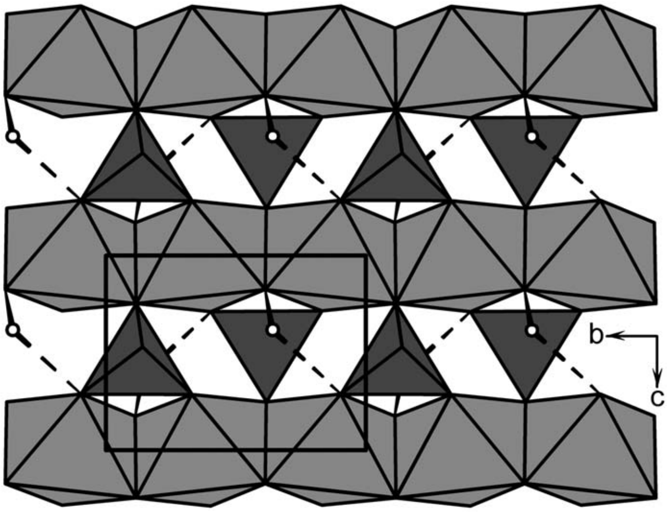

Fig. 3. View along [100] of one $[Ga(OH)PO_4]_\infty$ layer in $CsGa_2(OH)_2[(PO_4)H(PO_4)]$. See Fig. 1 for complete legend.

and O(4)–H(4)—O(2) angle of 144(3)° [29]. On the contrary, the O(3)—H(3)—O(3) bonds which exist between two layers correspond to very strong symmetric hydrogen bonds, as discussed above.

The Cs^+ cation interleaved between the layers is distributed over two sites, which are too close to each other to be occupied simultaneously. Most of the cesium atoms sit in the Cs(1) position in eight-fold coordination with Cs–O distances ranging from 3.073(2) to 3.293(2) Å, whereas a very small fraction sit in the Cs(2) position in nine-fold coordination, with Cs–O distances ranging from 2.439(10) to 3.577(10) Å.

As shown from their projections along ⟨001⟩ (Fig. 1) and ⟨010⟩ (Fig. 2), the phosphates $(NH_4)Ga(OH)PO_4$ [17] and $(en)Ga_2(OH)_2(PO_4)_2$ (*en* = ethylenediamine $[H_3N(CH_2)_2NH_3]^{2+}$) [18] exhibit closely related layered structures with that of $CsGa_2(OH)_2[(PO_4)H(PO_4)]$. The three structures indeed consist of $[Ga(OH)PO_4]_\infty$ layers interleaved with Cs^+ and H^+ (Fig. 1a and 2a), NH_4^+ (Fig. 1b and 2b) and en^{2+} (Fig. 1c and 2c) cations, respectively, but they are not isotypic. In order to compare more easily the three structures, the coordinates of $(en)Ga_2(OH)_2(PO_4)_2$ given in the original publication [18] have been transformed in the $P2_1/a$ space group and the origin have been shifted by (1/2, 0, 0). It thus appears that the structure of $(en)Ga_2(OH)_2(PO_4)_2$ can approximately be deduced from the one of $CsGa_2(OH)_2[(PO_4)H(PO_4)]$ by the operation of an additional 2 axis parallel to ***a***, for example, i.e. an element of symmetry not belonging to the point group of the two structures. This is clearly exemplified by the comparison of the (a) and (c) items of Figs. 1 and 2.

The $[Ga(OH)PO_4]_\infty$ layers of the organic and ammonium gallophosphates adopt very similar geometries compared to that of the cesium gallophosphate: the $[GaO_2(OH)_2]_\infty$ rutile ribbons are indeed interconnected through PO_4 tetrahedra in the same way. Such a great similarity of the layers of the three compounds is also shown by the ***b*** and ***c*** parameters which characterize the geometry of those layers: **b** of 5.987, 6.039 and 5.994 Å and **c** of 4.503, 4.488 and 4.464 Å for the cesium, ammonium and organic gallophosphates, respectively. However, one can notice small displacements of the oxygen atom corresponding to the free apex of PO_4 tetrahedra in the layers of the cesium and organic-templated phosphates. In particular, the latter compound presents the longest P–O bond of the three compounds (1.62 Å versus 1.57 and 1.58 Å in the cesium and ammonium phosphates, respectively). Compared with the most symmetric layer of the ammonium phase (Fig. 1b), a small distortion of the $[Ga(OH)PO_4]_\infty$ layer is observed with respect to ***a***, its tetrahedra being slightly tilted along ***b*** in the Cs and *en* phases (Fig. 1a and c, respectively). One can remark that these tilts are made in opposite ways (clockwise rotation on Fig. 1a and anti-clockwise on Fig. 1c). These distortions are correlated with a more fundamental characteristic of these two dimensional structures. The stability of the three structures is indeed ensured through hydrogen bonding between the free apex of the PO_4 tetrahedra in the $[Ga(OH)PO_4]_\infty$ layers and the inserted cations. The ammonium and *en* cations form four and three hydrogen bonds with neighboring layers, respectively, whereas cesium cannot form such bonds. This governed the relative positions of two successive layers as well as the distance between them.

As a matter of fact, one can observe that one $[Ga(OH)PO_4]_\infty$ layer out of two is shifted by about ***b***/4 in the Cs and *en* gallophosphates, compared to the ammonium phosphate (Fig. 1). In addition, the stacking along ***a*** of successive layers is made in opposite ways in the *en*-gallophosphate on one hand (Fig. 2c) and in the Cs and ammonium gallophosphates on the other hand (Fig. 2b and a, respectively). Consequently, the ***a*** parameter is about twice that of the ammonium phase, i.e. 16.07 and 18.54 Å for the Cs and *en* phases, respectively, against 8.50 Å for the ammonium phase. The spacing between the layers is, as expected, larger in the *en*-phosphate (9.27 Å) than in the two other compounds. However, this spacing is smaller in the Cs-phosphate (8.03 Å) than in the ammonium phosphate (8.50 Å), in spite of the larger size of the Cs^+ cations compared to NH_4^+ cation. This is easily explained by the facts that there are twice less Cs^+ cations than NH_4^+ cations between the layers and that no hydrogen bonds occur with cesium cations, so that two successive layers can thus be brought closer from each other. This is also evidenced by the distances between two free oxygen atoms of two successive layers: 3.67 and 2.39 Å for the NH_4^+ and Cs^+ compounds, respectively. An intermediate value of 3.41 Å is observed for the en^{2+} compound despite the largest spacing between its layers. This spacing is indeed compensated by the shift along ***b*** of two successive layers. Note that the charge of each $[Ga(OH)PO_4]^-$ layer is balanced by the intercalation of one NH_4^+ or $0.5(en^{2+})$ cation per layer in the ammonium and organic phases. In contrast, one observes only 0.5 Cs^+ cation per layer $[Ga(OH)PO_4]^-$ in the cesium phase, so that additional 0.5 H^+ per layer is required to ensure the charge balance. It is this additional hydrogen atom involving very short and symmetric hydrogen bonds between two successive layers through the PO_4 tetrahedra which stabilizes the 2D cesium phosphate. This trend seems to be evidenced by the numerous examples of such very strong symmetric hydrogen bonds in structures containing alkaline or alkaline-earth cations.

In conclusion, a new cesium hydroxyphosphate, $CsGa_2(OH)_2[(PO_4)H(PO_4)]$, with a layered structure has been synthesized. Its close structural relationships with $(NH_4)Ga(OH)PO_4$ and $(en)Ga_2(OH)_2(PO_4)_2$ through different hydrogen bonding modes suggest that it might be possible to control the distance between two $[Ga(OH)PO_4]_\infty$ layers, as well as their relative positions. Diamines with different carbon chain lengths, ammonium or cesium cations could coexist in the same matrix, leading to the formation of new derivatives.

Acknowledgments

The authors want to thank Jean-François Lohier for his kindful help. They gratefully acknowledge the Région Basse-Normandie and the Ministère de la Recherche for financial support.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.08.002.

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