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Crystal Structure of Mixed-metal Phosphite, $Pb_2Ga(HP^{III}O_3)_3(P^{V}O_3)$

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Abstract

One mixed-metal phosphite namely, $Pb_2Ga(HPO_3)_3(PO_3)$ (Compound 1) was obtained by a facile hydrothermal method and structurally characterized. Single crystal X-ray diffraction analysis reveals that crystallizes in the orthorhombic, space group Cmcm with unit cell dimensions, a=5.2572(12) Å, b=18.505(5) Å, c=12.544(3) Å and α=β=γ=90°. The crystal structure of $Pb_2Ga(HPO_3)_3(PO_3)$ exhibits a complicated 3D framework based on PbO_6 and GaO_6 octahedral connected by HPO_3 and H_2PO_3 anions via corner- or edge-sharing.

Keywords: Crystal structure; Hydrothermal reactions; Mixed-metal phosphites; 3D framework; Single-crystal X-ray diffraction

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Introduction

Metal phosphites have been paid more and more attention because of their abundant structures and potential applications in sorption, magnetism, photocatalyst and nonlinear optics [1-10]. Especially, pure inorganic metal phosphites with good thermostability and chemical stability have been exploited their application in various fields [9-13]. For example, two main-group metal phosphites, namely, $RbIn(HPO_3)_2$ [9] and $SnHPO_3$ [10], exhibit second harmonic generation (SHG) responses. Two alkali transition metal phosphites, namely, $Li_3Fe_2(HPO_3)_3Cl$ and $Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO_3)_6]1.5H_2O$, are good candidates of cathode materials [11,12]. In addition, a series of transition-metal (TM) phosphites exhibit different magnetic properties, such as $Na_2M(HPO_3)_2$ (M=Ni, Fe, Co) and A $[M(HPO_3)_2]$ (A=NH_4, K, Rb and M=V, Fe) [13,14]. The above-mentioned compounds display different properties with amazing structures due to the different connectivity modes between metal ions and phosphite anions. Thus, it is of vital importance and urgent to explore the structure of phosphite compounds to understand the relationship in the above mentioned properties. In view of the above mentioned discussion, new mixed-metal phosphite should been prepared and study the relationship between the crystal structural and the properties. Thus, here, we prepared the synthesis and crystal structure one new mixed-metal phosphite, namely, $Pb_2Ga(HPO_3)_3(PO_3)$.

Experimental

The starting materials were purchased from the Shanghai Reagent Factory (AR, 99.0%) without further purification.

Synthesis of $Pb_2Ga(HPO_3)_3(PO_3)$

A mixture of PbO (1 mmol), Ga_2O_3 (0.3 mmol), H_3PO_3 (2.5 mmol) and H_2O (5 mL) was sealed in an autoclave equipped with a Teflon liner (25 mL) and heated at 180°C for three days followed by being slowly cooled to room temperature at a rate of 5°C/h. The initial and final pH values of the solution were about 0.5 and 1, respectively. Single crystals suitable for X-ray diffraction studies were obtained and the product was colorless prism-shaped crystals.

Data collection

X-ray diffraction data collection for $Pb_2Ga(HPO_3)_3(PO_3)$ was performed on a Rigaku Mercury CCD diffractometer with Mo-Kα radiation (λ=0.71073 Å) at 293(2) K. The data sets were corrected for Lorentz and polarization factors as well as absorption by the multi-scan method [15-17]. The structure was solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [18,19]. All non-hydrogen atoms were

refined with anisotropic thermal parameters. According to the charge balance and bond valence calculations, all the H atoms in $Pb_2Ga(HPO_3)_3(PO_3)$ were needed and assigned to P-H bonds, but they were not refined due to the difficulty in the determination of their precise locations. All atoms were refined with anisotropic thermal parameters except for O(1) and O(2) in $Pb_2Ga(HPO_3)_3(PO_3)$, which was refined with 'isor' instruction. If this constraint is not applied, the displacement parameters for O(1) and O(2) will be abnormally small. The P(2) atoms in this compound is disordered with the P(2)-P(2)' distance of 0.889(12) Å. And the structure was also checked for possible missing symmetry with PLATON. Crystallographic data and structural refinements are summarized in **Table 1.** Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters, important bond distances and angles are listed in **Tables 2 and 3,** respectively.

Results and Discussion

Structure solving and refinement

Compound 1, namely, $Pb_2Ga(HPO_3)_3(PO_3)$, crystallizes in the orthorhombic space group *Cmcm* (no. 63) and features a 3D framework formed by the interconnection of 2D layer of lead phosphites and gallium phosphites **(Figure 1).** The asymmetric unit of $Pb_2Ga(HPO_3)_3(PO_3)$ includes 11 independent non-H atoms, including one Pb, one Ga, three P and six O atoms, in addition, all atoms except O(5) lie in special positions. Pb(1) is six coordinated by six oxygens from five HPO_3 anions and one $P(1)O_4$ anion in a distorted pentagonal pyramid geometry, Ga(1) is also six coordinated by six oxygens from six HPO_3 anions in a octahedral geometry. And the Pb^{2+} ions shows stereochemically active lone pairs. The Pb–O and Ga-O distances range from 2.510(6) to 2.702(5) Å, 1.957 (5) to 1.966 (7) Å, respectively. All of these bond distances are comparable to those reported for other lead(II) phosphites [20] and gallium phosphites [9,21]. The calculated total bond valences for Pb(1), Ga(1) and P(1) atoms are 1.671 3.025 and 5.430, respectively, indicating that Pb, Ga and P(1) are in oxidation states of +2, +3 and +5, respectively, in accordance with the crystal structure results. P(1) atom is coordinated with two O(1) and two O(2) atoms to form $[PO_4]^{3-}$ tetrahedral units, and the occupancy of P(1), O(1) and O(2) is 25%, 25% and 50%, respectively, while P(2) and P(3) atoms bond to three oxygen atoms and one hydrogen atom, forming the pseudo-tetrahedral coordination geometry. The presence of $P(1)O_4$ phosphates might be due to the H_3PO_3 is oxidized in the reaction progress. The P–O bond distances range from 1.486 (9) to 1.528(5) **(Table 2)**. The phosphates and phosphites anions adopt different coordination modes. $P(1)O_4$ phosphates shows a μ_4-$\eta^2\eta^2$-coordination mode that bridges 4Pb atoms with two O atoms, $HP(2)O_3$ anion displays 4.211 coordination mode that bridges 4Pb atoms, and $HP(3)O_3$ anion adopts 5.221 coordination mode that bridges 5Pb atoms. The PbO_6 octahedra and HPO_3 and PO_4 anions are interconnected via edge-sharing into a novel 2D anionic network in the *ac* palne with the 6-member rings tunnels along *b*-axis **(Figure 2).** While, the GaO_6 octahedra and HPO_3 pseudo-tetrahedra are interconnected via vertex-sharing resulting in a 2D anionic network in the *ac* palne with the 4-Member Rings tunnels along *b*-axis **(Figure 3).** Such two type of 2D layers further bridges by corner-sharing oxygen atom to yield a 3D framework in the *ab* plane (**Figure 1**).

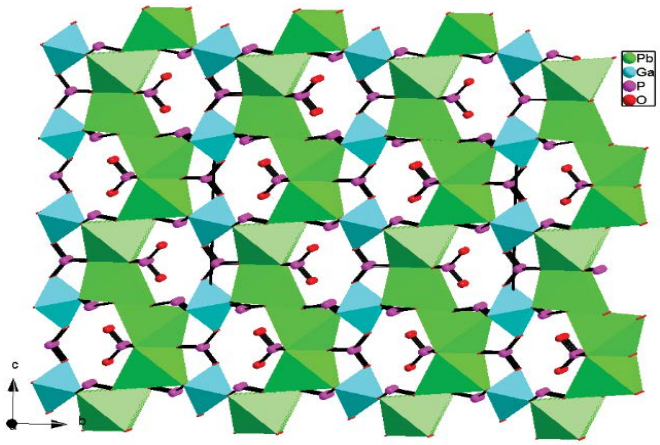

Figure 1 View of structure of compound **1** perpendicular to the *a* axis, the green and blue polyhedra represent the PbO_6 and GaO_6 octahedra, respectively.

Table 1 Crystal data and structural refinement for $Pb_2Ga_2(HPO_3)_3(H_2PO_3)$.

Compound	1
Empirical formula	$Pb_2Ga(HPO_3)_3(PO_3)$
Formula weight	833.97
Temperature	293(2) K
Crystal system	Orthorhombic
Space group	Cmcm
a/Å	5.2572(12)
b/Å	18.505(5)
c/Å	12.544(3).
V/Å^3	1220.3(5)
Z	4
D_c/g·cm^{-3}	4.539
μ (Mo Kα)/m^{m-}1	30.432
F(000)	1484
Reflections collected/unique	5010/809 [R(int)=0.0602]
Completeness to theta=27.46	99.4 %
Data/restraints/parameters	809/6/65
Goodness-of-fit on F^2	1.183
Final R indices [I>2sigma(I)] [a]	R_1=0.0333, wR_2=0.0686
R indices (all data)	R_1=0.0355, wR_2=0.0696
Extinction coefficient	0.00091(9)
Largest diff. peak and hole	1.813 and -1.714 e. Å^{-3}

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $\omega R_2=\{\Sigma\omega[(F_o)^2(F_c)^2]^2/\Sigma\omega[(F_o)^2]^2\}^{1/2}$

Conclusions

In summary, we reported one new mixed-metal phosphites, namely, $Pb_2Ga(HPO_3)_3(PO_3)$ using a facile hydrothermal method

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for the non-hydrogen atoms of $Pb_2Ga(HPO_3)_3(H_2PO_3)$.

Atoms	x	y	z	U(eq)
Pb(1)	5000	1900(1)	1004(1)	15(1)
Ga(1)	5000	0	5000	8(1)
P(1)	0	2841(2)	2500	12(1)
P(2)	4155(11)	200(3)	2500	12(1)
P(3)	5000	3924(1)	190(2)	9(1)
O(1)	0	3338(8)	3470(11)	11(3)
O(2)	2370(19)	2403(5)	2500	33(2)
O(3)	5000	987(6)	2500	18(2)
O(4)	5000	-231(4)	3470(6)	16(2)
O(5)	2581(10)	4260(3)	-269(4)	14(1)
O(6)	5000	3119(4)	-65(7)	19(2)

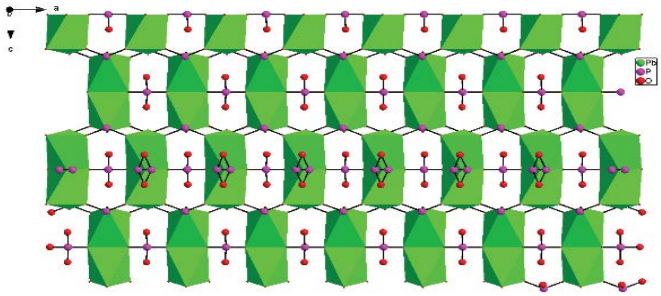

Figure 2 2D layer constructed from lead(II) phosphites perpendicular to the *b* axis.

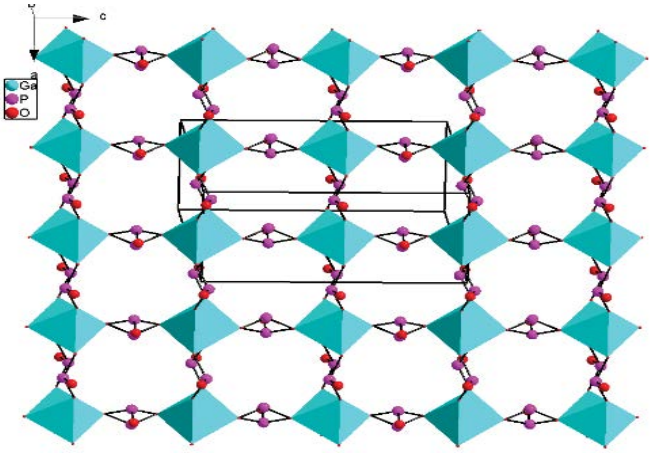

Figure 3 2D layer constructed from gallium (II) phosphites in the *ac* plane.

and it crystallizes in the orthorhombic space group *C*mcm, which features 3D framework formed by the interconnection of 2D layer of lead(II) phosphites and 2D layer of gallium(III) phosphites. Our future research efforts will be devoted to the design and preparation of different mixed-metal phosphites with d^0-transition metals such as Ti^{4+}, V^{5+} and Mo^{6+} to exploit this related systems and study the relationship between the crystal structures and properties of this related materials.

Acknowledgements

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Table 3 Bond distances (Å) and angles [°] for $Pb_2Ga(HPO_3)_3(PO_3)$.

Pb(1)-O(2)#1	2.510(6)	Ga(1)-O(5)#5	1.957(5)
Pb(1)-O(2)	2.510(6)	Ga(1)-O(5)#6	1.957(5)
Pb(1)-O(3)	2.525(7)	Ga(1)-O(5)#7	1.957(5)
Pb(1)-O(6)	2.624(7)	Ga(1)-O(4)	1.966(7)
Pb(1)-O(5)#2	2.702(5)	Ga(1)-O(4)#8	1.966(7)
Pb(1)-O(5)#3	2.702(5)	P(1)-O(2)#9	1.486(9)
Ga(1)-O(5)#4	1.957(5)	P(1)-O(2)	1.486(9)
P(1)-O(1)	1.525(14)	P(3)-O(5)#1	1.528(5)
P(1)-O(1)#10	1.525(14)	P(2)-O(4)#10	1.521(8)
P(3)-O(6)	1.525(7)	P(2)-O(4)	1.521(8)
P(3)-O(5)	1.528(5)	P(2)-O(3)	1.522(12)
O(2)#1-Pb(1)-O(2)	66.9(4)	O(5)#4-Ga(1)-O(5)#5	87.8(3)
O(2)#1-Pb(1)-O(3)	72.1(2)	O(5)#4-Ga(1)-O(5)#6	180.0(2)
O(2)-Pb(1)-O(3)	72.1(2)	O(5)#5-Ga(1)-O(5)#6	92.2(3)
O(2)#1-Pb(1)-O(6)	93.6(2)	O(5)#4-Ga(1)-O(5)#7	92.2(3)
O(2)-Pb(1)-O(6)	93.6(2)	O(5)#5-Ga(1)-O(5)#7	180.000(1)
O(3)-Pb(1)-O(6)	162.8(3)	O(5)#6-Ga(1)-O(5)#7	87.8(3)
O(2)#1-Pb(1)-O(5)#2	145.7(2)	O(5)#4-Ga(1)-O(4)	90.9(2)
O(2)-Pb(1)-O(5)#2	105.9(3)	O(5)#5-Ga(1)-O(4)	90.9(2)
O(3)-Pb(1)-O(5)#2	73.85(19)	O(5)#6-Ga(1)-O(4)	89.1(2)
O(6)-Pb(1)-O(5)#2	120.56(19)	O(5)#7-Ga(1)-O(4)	89.1(2)
O(2)#1-Pb(1)-O(5)#3	105.9(3)	O(5)#4-Ga(1)-O(4)#8	89.1(2)
O(2)-Pb(1)-O(5)#3	145.7(2)	O(5)#5-Ga(1)-O(4)#8	89.1(2)
O(3)-Pb(1)-O(5)#3	73.85(19)	O(5)#6-Ga(1)-O(4)#8	90.9(2)
O(6)-Pb(1)-O(5)#3	120.56(19)	O(5)#7-Ga(1)-O(4)#8	90.9(2)
O(5)#2-Pb(1)-O(5)#3	60.3(2)	O(4)-Ga(1)-O(4)#8	180.000(1)
P(2)#1-P(2)-O(4)#10	73.0(2)	O(2)#9-P(1)-O(2)	113.9(9)
P(2)#1-P(2)-O(4)	73.0(2)	O(2)#9-P(1)-O(1)	109.2(3)
O(4)#10-P(2)-O(4)	106.2(6)	O(2)-P(1)-O(1)	109.2(3)
P(2)#1-P(2)-O(3)	73.0(2)	O(2)#9-P(1)-O(1)#10	109.2(3)
O(4)#10-P(2)-O(3)	114.6(4)	O(2)-P(1)-O(1)#10	109.2(3)
O(4)-P(2)-O(3)	114.6(4)	O(1)-P(1)-O(1)#10	105.9(11)
O(6)-P(3)-O(5)	108.6(3)	O(6)-P(3)-O(5)#1	108.6(3)
		O(5)-P(3)-O(5)#1	112.7(4)

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Additional Information

Crystallographic data for the structures reported here can be obtained from the FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, Fax: +497247808666; E-mail: crysdata@fiz-karlsruhe.de on quoting the depository numbers CSD 430503.

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