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A new congruent-melting double phosphate $PbCd(PO_3)_4$ with photocatalytic activity

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ABSTRACT

By combining Pb^{2+} with ds-block elements, a new double phosphate $PbCd(PO_3)_4$ has been synthesized for the first time. It crystallizes in space group $P2_1/n$ of the monoclinic system with unit cell parameters of $a = 7.1191\ (14)$ Å, $b = 9.0871\ (18)$ Å, $c = 14.681\ (3)$ Å, $\beta = 91.40\ (3)^\circ$ and $Z = 4$. Its structure contains $^{\infty}_{1}[PO_3]$ chains running along the a direction, which are further bridged by isolated $[CdO_6]$ triangular prisms to generate a 3D framework with Pb^{2+} cations filling in the cavities. Based on UV-vis-NIR spectroscopy measurement, $PbCd(PO_3)_4$ has a large band gap of 4.85 (2) eV, which is consistent with the density functional theory (DFT) study. In addition, the DSC curve demonstrates that $PbCd(PO_3)_4$ melts congruently at 727 °C. Additionally, the title compound displays a UV-photocatalytic activity to decompose RhB under 500 W mercury lamp ($\lambda = 256$ nm) radiation about 0.62 times that of P25 (TiO_2).

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1. Introduction

Over the past decades, metal phosphates have attracted significantly interest due to their potential applications in the realm of magnetism, catalysis, piezoelectricity and nonlinear optics [1–8]. as well as for the intriguing compositional and structural diversity [9–11]. Recently, metal phosphates containing the group IVA elements, in particular the Pb metal, have received increasing interest [12–15]. The element Pb, which is usually stabilized in +2 oxidation state with stereochemically active $6s^2$ lone pair electrons, shows various coordination geometries and hence results in diverse structure types with fascinating properties. For instance, the structure of $Pb_3Bi(PO_4)_3$ [13] contains a three-dimensional network formed by strongly distorted mixed $[(Pb/Bi)O_6]$ octahedra connected by edge-sharing to generate corrugated chains which are linked by $[PO_4]$ tetrahedra via corner-sharing. It exhibits phase-matchable NLO property with a powder second harmonic generation signal about 3.0 times that of KH_2PO_4 (KDP). Another example is the lead chromium phosphate $Pb_3Cr_2(PO_4)_4$ [14], which contains two polymorphic phases, namely, the monoclinic phase and the tetragonal phase. The study of the phase relation shows that only small changes take place in the construction of the $[Cr_2(PO_4)_4]$ framework of those two phases, which may be caused by the different coordination environment of the Pb^{2+} ions.

On the other hand, extensive work on metal phosphates has been focused on introducing transition metal ions in d-block. Examples include $LiFePO_4$ [16], $LiMnPO_4$ [17], and $LiCoPO_4$ [18], which are all served as outstanding lithium ion battery cathode materials, and $PbFe_3O(PO_4)_3$ [12], $Na_2Ni(HPO_3)_2$ [19], $Na_4NiFe(PO_4)_3$ [20] and $Na_2Ni_2Fe(PO_4)_3$ [20], which exhibit interesting magnetic properties, and $(VO)_2P_2O_7$ [21] and $M_{0.5(1+x)}Cr_xTi_{2-x}(PO_4)_3$ (M = Mg, Ca, Mn, Ni, Sr, Ba, Pb) [22], which display good catalytic performances, *etc.* In contrast, the exploration in ds-block elements-containing metal phosphates is relatively scarce. The strong polarization ability of ds-block cations make them extremely susceptible to second-order Jahn-Teller (SOJT) effect and rather easy to form varieties of compounds with interesting anion groups, such as the $[ZnO_4]$

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tetrahedra in $KZn_4(PO_4)_3$ [23] and $Rb_2Zn_3(P_2O_7)_2$ [24], the $[ZnO_5]$ square pyramids in β-$Zn_3P_2O_8$ [25], the $[CuO_4]$ planar quadrilateral in Li_3CuO_3 [26], and $[CdO_8]$ polyhedra in $Cd_2Nb_2O_7$ [27].

If the p-block Pb and ds-block elements can be incorporated into one compound, the interplay between cations with different electronic configuration and coordination preference may lead to new compounds with interesting structures and properties. Inspired by the above strategy, we have focused our main attention on the Pb–M–P–O (M = Cu, Ag, Zn, Cd) system and successfully discovered a new compound $PbCd(PO_3)_4$, which crystallizes in space group $P2_1/n$ of the monoclinic system. Its structure features a 3D framework formed by corner-sharing $^{\infty}_{1}[PO_3]$ chains and isolated $[CdO_6]$ triangular prisms with Pb^{2+} cations occupying the cavities. Both experimental result and density functional theory (DFT) study indicate that $PbCd(PO_3)_4$ is a typical insulator with a large band gap of 4.85 (2) eV. Additionally, $PbCd(PO_3)_4$ melts congruently at 727 °C. Moreover, stimulated by numerous results that many compounds containing cations with electron lone pair exhibit excellent photocatalytic activities [28–30], subsequently we investigated the photocatalytic performance of $PbCd(PO_3)_4$. Interestingly, the title compound displays a UV-photocatalytic activity to decompose RhB under 500 W mercury lamp (λ = 256 nm) irradiation about 0.62 times that of P25. Here, we report the synthesis, structural characterization, thermal, optical and photocatalytic properties of $PbCd(PO_3)_4$.

2. Experimental section

2.1. Synthesis

The following reagents were used as obtained: PbO (Sinopharm Chemical Reagent Co., Ltd., 99.9%), CdO (Sinopharm Chemical Reagent Co., Ltd., 99%), $NH_4H_2PO_4$ (Sinopharm Chemical Reagent Co., Ltd, 99.9%), polycrystalline sample of $PbCd(PO_3)_4$ was obtained by traditional solid state reaction with a stoichiometric mixture of PbO, CdO, and $NH_4H_2PO_4$. The raw materials were carefully ground and mixed in an agate mortar and packed into a platinum crucible, and then were heated in a muffle furnace to 473 K in the first round to ensure the decomposition of $NH_4H_2PO_4$. The mixture was ground thoroughly and heated gradually to 773 K over two days with several grindings, until the pure single phase powders with white color were obtained.

2.2. Crystal growth

Single crystals of $PbCd(PO_3)_4$ were achieved by the flux method through spontaneous crystallization using excessive $NH_4H_2PO_4$ as flux. Reaction mixtures of PbO, CdO and $NH_4H_2PO_4$ in a molar ratio of 1:1:5 were homogeneously mixed and placed in a platinum crucible, then gradually heated in a computer-controlled furnace until they melted. The melted sample was kept at that temperature for at least 12 h, and then slowly cooled at a rate of 3 °C/h, finally cooled to room temperature by switching off the furnace. The product consisted of colorless block crystals, which were manually selected for structure characterization.

2.3. Structure determination

Single-crystal X-ray diffraction experiment was performed on a Rigaku AFC10 diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at 293 K. The collection of the intensity data and cell refinement was carried out with Crystalclear software [31]. Multi-scan absorption corrections were performed numerically with the use of the program XPREP [32].

The structure was solved with the direct methods SHELXTLS program and refined with the least-squares program SHELXL of the SHELXTL.PC suite of programs [32]. The crystal data and structural refinement for $PbCd(PO_3)_4$ are given in Table 1. Selected bond distances are given in Table 2. Positional coordinates and equivalent isotropic displacement parameters for the title compound are given in Table 3. Further information may be found in Supplementary Material.

2.4. Powder X-ray diffraction (PXRD) and thermal analysis [differential scanning calorimetry (DSC)]

The PXRD pattern of the ground powder was performed at room temperature on a Bruker D8 Focus diffractometer with Cu Kα (λ = 1.5418 Å) radiation. The scanning step width of 0.05° and a fixed counting time 0.2 s/step were applied to record the patterns in the 2θ range of 10–70°. The measured XRD powder pattern was found to perfectly match the simulated pattern generated using the CIF of the refined structures. (Fig. 1).

The thermal property of $PbCd(PO_3)_4$ was investigated by the differential scanning calorimetric (DSC) analysis using the LabsysTM TG-DTA16 (SETARAM) thermal analyzer calibrated with Al_2O_3. A polycrystalline sample (~30 mg) was placed in a platinum crucible and heated from room temperature to 750 °C at a rate of 15 °C/min in a nitrogen atmosphere.

Table 1
Crystal data and structure refinement for $PbCd(PO_3)_4$.

Chemical content	$PbCd(PO_3)_4$
Fw	635.47
a(Å)	7.1191 (14)
b(Å)	9.0871 (18)
c(Å)	14.681 (3)
β(°)	91.40 (3)
Space group	$P2_1/n$
V (Å^3)	949.4 (3)
Z	4
T(K)	293 (2)
λ(Å)	0.71073
ρ_c (g/cm^3)	4.446
μ(mm^{-1})	20.690
$R(F)^a$	0.0435
$R_W(F_o^2)^b$	0.0715

[a] $R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_W(F_o^2) = \{\Sigma\ [w\ (F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (zP)^2$, where $P = (\mathrm{Max}\ (F_o^2, 0) + 2F_c^2)/3$.

Table 2
Selected bond lengths(Å) for $PbCd(PO_3)_4$.

$PbCd(PO_3)_4$			
P1—O3	1.496 (5)	P1—O6	1.607 (5)
P1—O7	1.578 (5)	P1—O11	1.494 (5)
P2—O1	1.603 (5)	P2—O4	1.491 (6)
P2—O7	1.591 (5)	P2—O8	1.492 (5)
P3—O5	1.474 (5)	P3—O6	1.599 (5)
P3—O9	1.593 (5)	P3—O10	1.487 (5)
P4—O1	1.586 (6)	P4—O2	1.492 (6)
P4—O9	1.593 (5)	P4—O12	1.473 (5)
Pb—O2	2.751 (5)	Pb—O3	2.645 (5)
Pb—O4	2.780 (5)	Pb—O5	2.498 (5)
Pb—O8	2.758 (5)	Pb—O10	2.879 (4)
Pb—O11	2.711 (5)	Pb—O12	2.461 (5)
Cd—O2	2.256 (5)	Cd—O3	2.268 (5)
Cd—O4	2.277 (5)	Cd—O8	2.290 (4)
Cd—O10	2.289 (5)	Cd—O11	2.326 (5)