



## Syntheses, characterization and theoretical studies of three apatite-type phosphates $MPb_4(PO_4)_3$ ( $M = K, Rb, Cs$ )



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### ABSTRACT

Three phosphates  $MPb_4(PO_4)_3$  ( $M = K, Rb, Cs$ ) have been synthesized by the high temperature melt method. The single-crystal X-ray structural analyses reveal that all of them belong to apatite-type phases and crystallize in the same space group,  $P6_3/m$  (no. 176). They exhibit a three dimensional (3D) structure that is composed of two kinds of channels constructed by  $[Pb(1)O_6]$  and  $[PO_4]$ . And the  $[Pb(2)|K(1)]$  ( $[Pb(2)|Rb(1)]$ ,  $[Pb(2)|Cs(1)]$ ) atoms are located in the small channels. Detailed structural comparison indicates that the cations effect on the framework geometry is less obvious among the title compounds and the reported lead apatite-type phosphates, however, although  $MPb_4(PO_4)_3$  ( $M = K, Rb, Cs$ ) have the similar stoichiometry with  $MM'_4(BO_3)_3$ , the different coordination of the B and P atoms, as well as the cations effect make  $MPb_4(PO_4)_3$  and  $MM'_4(BO_3)_3$  crystallize in various space groups. The IR spectra were used to verify the validity of their structure. The TG-DSC analysis results indicate that  $KPb_4(PO_4)_3$  and  $RbPb_4(PO_4)_3$  melt congruently. The UV–Vis–NIR diffuse reflectance spectra indicate that they have no obvious absorption from 300 to 2500 nm. Optical properties as well as band structure calculations have been also performed based on density functional theory methods.

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## 1. Introduction

Design and discovery of new materials that can be used in different areas of science and technology are attracted much attention as one of hot research issues. Many strategies and methods have been used to synthesize new compounds. For example, oxyfluoride groups are used to design polar materials by Poeppelmeier et al. [1]; new oxide materials with second-order Jahn-Teller distortions were reported by Halasyamani and Mao et al. [2,3]; new compounds with polar chalcogenide units like  $[AsS_3]^{3-}$ ,  $[SbS_3]^{3-}$ , and  $[TeS_3]^{2-}$  were obtained by Kanatzidis et al., and so on [4–7]. One of the most representative strategies to the synthesis of novel oxides are focused on the borates due to their unique structures and excellent performances. During the past

several decades, extensive studies on borate crystals have produced a large number of crystals with multifunctional physical and chemical properties, such as  $BaB_2O_4$  (BBO),  $KBe_2BO_3F_2$  (KBBF),  $Na_3Ba_2(B_3O_6)_2F$  (NBBF),  $YCa_4O(BO_3)_3$  (YCOB) and so on [8–11].

In crystal engineering, modification of the crystal structure by substitution of  $BO_3$  and  $PO_4$  is one of the efficient methods to obtain new structures with different properties, such as  $Ca_5(BO_3)_3F$  and  $Ca_5(PO_4)_3F$  [12],  $Co_3(BO_3)_2$ ,  $Co_3(PO_4)_2$  and  $Co_3(BO_3)(PO_4)$  [13],  $Mg_3(BO_3)_2$ ,  $Mg_3(PO_4)_2$  and  $Mg_3(BO_3)(PO_4)$  [14]. Of course metal phosphates have also attracted great interest for designing new optical materials since the discovery of  $Ba_3P_3O_{10}X$  ( $X = Cl, Br$ ) [15],  $RbBa_2(PO_3)_5$ ,  $Rb_2Ba_3(P_2O_7)_2$  [16] and  $Ba_3(ZnB_5O_{10})PO_4$  [17], and so on [18]. Inspired by the above idea, we tried to substitute  $BO_3$  using  $PO_4$  in noncentrosymmetric  $MM'_4(BO_3)_3$  ( $M = Na, M' = Ca$  and  $M = K, M' = Ca, Sr$ ) [19], expecting to explore novel compounds and investigate structural changes after the substitution. In addition, considering the highly bonding feature of  $Pb^{2+}$  resulted from its stereochemically active lone-pair electrons, we also introduced Pb in the compounds. After our systematic efforts, three lead apatite-type phosphates  $MPb_4(PO_4)_3$  ( $M = K, Rb, Cs$ ) were produced. Hence,

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in this paper, synthesis, crystal structure and structure comparison among the three compounds and other related compounds are reported. Meanwhile, characterizations including TG-DSC analysis, infrared spectra, UV–Vis–NIR diffuse reflectance spectra of three compounds, as well as electronic structure and linear optical calculations of  $\text{RbPb}_4(\text{PO}_4)_3$  are also presented. To date, theoretical calculation and experimental study on the linear optical properties of lead apatite-type phosphates have not been documented. The birefringence of the crystals were calculated from their band structures. These results are very useful to the design and search for new crystals with specific physical and chemical properties.

## 2. Experimental section

### 2.1. Solid-state synthesis

Polycrystalline samples of three compounds were synthesized via conventional solid state reactions with stoichiometric amounts of  $\text{K}_2\text{CO}_3/\text{Rb}_2\text{CO}_3/\text{Cs}_2\text{CO}_3$ ,  $\text{PbO}$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The mixtures were heated to  $400^\circ\text{C}$  and dwelled for 12 h in a muffle furnace. The mixtures were cooled to room temperature and finely ground again. Then the mixtures were sintered at  $720^\circ\text{C}$  ( $\text{KPb}_4(\text{PO}_4)_3$  and  $\text{RbPb}_4(\text{PO}_4)_3$ ),  $650^\circ\text{C}$  ( $\text{CsPb}_4(\text{PO}_4)_3$ ), respectively.

The phase purity was confirmed by powder X-ray diffraction (XRD) pattern. The powder XRD data were carried out with a Bruker D2 PHASER diffractometer using monochromatized  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The diffraction patterns were performed in the angular range of  $2\theta = 5\text{--}80^\circ$  with a scan step width of  $0.02^\circ$  and a fixed counting time of 1 s per step. The diffraction patterns are in good agreement with the calculated ones. (Figure S1 in the Supporting Information (SI)).

### 2.2. Crystal growth

Single crystals of  $\text{MPb}_4(\text{PO}_4)_3$  ( $M = \text{K}, \text{Rb}, \text{Cs}$ ) were obtained through spontaneous crystallization from high-temperature melt. To  $\text{KPb}_4(\text{PO}_4)_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{PbO}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in a molar ratio of 1: 8: 6 were mixed and ground in an agate mortar. Then the well mixed powder was put in the platinum crucible, which was put in the vertical, programmable temperature furnace. The furnace was heated to  $980^\circ\text{C}$  and held for 2 h at this temperature, then cooled to  $800^\circ\text{C}$  at  $3^\circ\text{C/h}$ . Finally, the melt was quickly cooled down to room temperature at  $10^\circ\text{C/h}$ . During the slow cooling process, colorless single crystals were obtained successfully. Crystals of  $\text{RbPb}_4(\text{PO}_4)_3$  and  $\text{CsPb}_4(\text{PO}_4)_3$  were successfully obtained under the similar process.

### 2.3. Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected at  $296(2) \text{ K}$  on an APEX II CCD diffractometer using monochromatic  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and integrated with the SAINT program [20]. The structure was determined by the direct methods and refined by full-matrix least-squares fitting on  $F_o^2$ . All the calculations were performed with programs from the SHELXTL crystallographic software package [21a]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was checked with PLATON for missing symmetry elements [21b]. Crystal data, details of data collections, and structure refinement information are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are summarized in Table S1 in the SI. The selected bond lengths and angles are listed in Table S2 in the SI.

### 2.4. Infrared spectra

Infrared spectra of the samples were recorded on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the range from  $400$  to  $4000 \text{ cm}^{-1}$  at room temperature. The sample was mixed thoroughly with dried KBr (5 mg of the sample and 500 mg of KBr).

### 2.5. Thermal behavior analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with NETZSCH STA 449F3 simultaneous thermal analyzer instrument. The sample and reference ( $\text{Al}_2\text{O}_3$ ) were enclosed in Pt crucibles, and heated from  $40$  to  $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C/min}$  under a nitrogen atmosphere.

### 2.6. UV–Vis–NIR diffuse reflectance spectra

The Shimadzu SolidSpec-3700DUV spectrophotometer is used to measure the spectra of powder sample over a  $190$  to  $2600 \text{ nm}$  wavelength range. Reflectance spectra are converted to absorbance with the Kubelka-Munk function [22].

### 2.7. Numerical calculation details

To analyze the electronic structure and the relationship between optical properties and crystal structure, a plane-wave pseudopotential method based on density functional theory (DFT) calculation was performed using the CASTEP module [23]. During the calculation, geometry optimization was performed using the BFGS minimization technique. The geometry optimization was converged criterion that the residual forces on the atoms were less than  $0.01 \text{ eV/\AA}$ , the displacements of atoms were less than  $5 \times 10^{-4} \text{ \AA}$ , and the energy change was less than  $5.0 \times 10^{-6} \text{ eV/atom}$ . The exchange-correlation functional was adopted by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional. The interactions between the ionic cores and the electrons were described by Norm conserving (NCP) pseudopotentials [24]. The orbital electrons treated as valence electrons were  $\text{Rb}: 4s^2 4p^6 5s^1$ ,  $\text{Pb}: 5s^2 5p^6 5d^{10} 6s^2 6p^2$ ,  $\text{P}: 3s^2 3p^3$ ,  $\text{O}: 2s^2 2p^4$ . The energy cutoff of the plane-wave basis was set at  $910 \text{ eV}$  and the k-point grid sampling in the Monkhorst-Pack scheme was set at  $3 \times 3 \times 2$  with a separation of  $0.04 \text{ \AA}^{-1}$  in the Brillouin zone. The default values of the CASTEP code were retained, along with the other calculation parameters and convergent criteria. The linear optical properties of the crystal were examined through calculating the complex dielectric function  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ . The imaginary part of the dielectric function  $\epsilon_2$  is given in the following equation [25a]:

$$\epsilon_2(q \rightarrow 0, h\omega) = \frac{2e^2\pi}{\Omega\epsilon_0} |\langle \varphi_k^c | u \cdot r | \varphi_k^v \rangle|^2 \delta[E_k^c - E_k^v - E]$$

The real part  $\epsilon_1(\omega)$  can be obtained from the imaginary part  $\epsilon_2(\omega)$  by the Kramers–Kronig transformation. All the other optical constants, such as the absorption spectrum, refractive index, and reflectivity are derived from  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  [25b].

## 3. Results and discussion

### 3.1. Crystal structure

$\text{MPb}_4(\text{PO}_4)_3$  ( $M = \text{K}, \text{Rb}, \text{Cs}$ ) crystallize in space group  $P6_3/m$  (no. 176) of the hexagonal system. The crystal structure of  $\text{KPb}_4(\text{PO}_4)_3$  is same with that of  $\text{K}_2\text{Pb}_8(\text{PO}_4)_6$  reported by Mathew in 1980 [26].

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