



Crystal and band structure of $K_2AlTi(PO_4)_3$ with the langbeinite-type structure

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ABSTRACT

Solid-state reaction of K_2CO_3 , Al_2O_3 , TiO_2 and $NH_4H_2PO_4$ at $1000^\circ C$ leads to a new dipotassium aluminum titanium phosphate: $K_2AlTi(PO_4)_3$. Its structure was established by single-crystal X-ray diffraction. The title compound crystallizes in the cubic space group $P2_13$ (No. 198) with cell parameters of $a = 9.76410(10) \text{ \AA}$ and $V = 930.886(17) \text{ \AA}^3$. It belongs to the langbeinite $[K_2Mg_2(SO_4)_3]$ structure type and its structure features a three-dimensional anionic network of $[AlTi(PO_4)_3]^{2-}$ interconnected by K^+ cations. The elemental analysis, IR spectrum and UV-vis absorption spectrum have been investigated. Additionally, we also make the calculations of band structure and density of states with the density functional theory method for the title compound.

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1. Introduction

With the development of technology and science, there is an increasing need for new multifunctional magnetic materials, ultra-violet (UV) phosphors, scintillators, and laser materials, which have extensive applications in several domains [1–9]. Coordination networks based on $[M_2(PO_4)_3]$ fragment may result in diverse structure types with consequent interesting magnetism, electricity, optic and thermal expansion properties. The basic unit of these compounds consists of MO_6 octahedra and PO_4 tetrahedra interconnected by alkali metals or alkali-earth metals. Introduction a variety of cations (Mg^{2+} , Al^{3+} , Si^{4+} , Ge^{4+} , Ti^{4+} , Zr^{4+} , Y^{3+} , Nb^{5+} , Er^{3+} , etc.) into M sites led to the formation of several different structures, such as Nasicon-type, garnet-type and langbeinite-type. So far, the langbeinite-type phosphates reported include $KBaFe_2(PO_4)_3$ [10], $K_2Ti_2(PO_4)_3$ [11], $K_2MTi(PO_4)_3$ ($M = Er, Yb$ or Y) [12], $K_2FeZr(PO_4)_3$ [13], $K_2Mn_{0.5}Ti_{1.5}(PO_4)_3$ [14], $K_2SnX(PO_4)_3$ ($X = Fe, Yb$) [15], $Na_2MTi(PO_4)_3$ ($M = Fe, Cr$) [16], etc. Slobodyanik et al. have reported the crystal structure of compounds $K_{1.388}Ti_{1.885}Al_{0.115}(PO_4)_3$ [17]. In this work, we will present the synthesis, crystal structure determination, as well as the calculations of crystal energy band structures of stoichiometric species $K_2AlTi(PO_4)_3$.

2. Experimental

2.1. Materials and instrumentation

All of the chemicals, K_2CO_3 , Al_2O_3 , TiO_2 , $NH_4H_2PO_4$, were purchased from Shanghai Reagent Factory, and they were analytically pure from commercial sources and used without further purification. Microprobe elemental analyses on K, Al, Ti and P elements were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). X-ray powder diffraction (XRD) pattern ($Cu K\alpha$) was collected on a X'PERT-MPD θ - 2θ diffractometer. The IR spectrum was recorded on a Magna 750 FT-IR spectrometer photometer as a KBr pellet in the 1600 – 400 cm^{-1} . Optical diffuse reflectance spectrum was measured with a PE Lambda 900 UV-vis spectrophotometer in the wavelength range of 200 – 800 nm at room temperature. The instrument was equipped with an integrating sphere and controlled by a personal computer. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were determined by the diffuse-reflectance technique. $F(R)$ and R are linked by $F(R) = (1 - R)^2 / 2R$, where R is the reflectance and $F(R)$ is the Kubelka–Munk remission function. The minima in the second-derivative curves of the Kubelka–Munk function are taken as the position of the absorption bands.

2.2. Synthesis

Single crystal of $K_2AlTi(PO_4)_3$ was initially obtained by the high temperature solid-state reaction of K_2CO_3 (1.352 g, 9.783 mmol), Al_2O_3 (0.1663 g, 1.630 mmol), TiO_2 (0.2605 g, 3.261 mmol) and $NH_4H_2PO_4$ (3.000 g, 26.09 mmol), with the molar ratio of 6:1:1:8 (K:Al:Ti:P). The reaction mixture was thoroughly ground in an agate mortar and pressed into a pellet to ensure the best homogeneity and reactivity, which was put into a platinum crucible and calcined at $400^\circ C$ for 10 h to decompose the salt. Then the crucible was transferred to an oven and heated at $900^\circ C$ for 48 h. Then the sample was cooled from 900 to $25^\circ C$ at a rate of $6^\circ C/h$. A few prism-shaped colorless crystals were obtained in very low yield (<5%). After proper structural analysis, a pure-powder sample of $K_2AlTi(PO_4)_3$ was obtained quantita-

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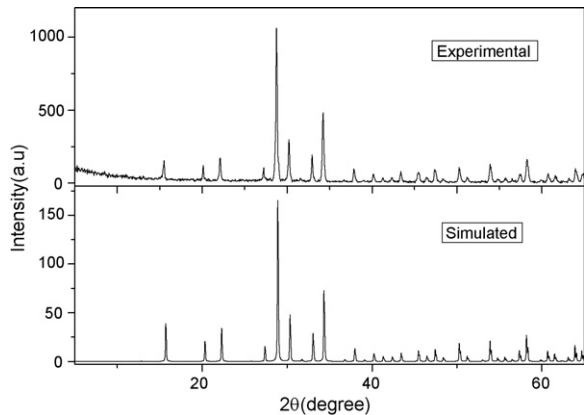


Fig. 1. Experimental and simulated X-ray powder diffraction patterns of $K_2AlTi(PO_4)_3$.

tively by the solid-state reaction of a mixture of $K_2CO_3/Al_2O_3/TiO_2/NH_4H_2PO_4$ in a molar ratio of 2:1:2:6 at 900 °C for 10 days. Its purity was confirmed by powder XRD studies (Fig. 1).

2.3. Crystal structure determination

A colorless prism crystal of $K_2AlTi(PO_4)_3$ with dimensions 0.10 mm × 0.05 mm × 0.05 mm was selected and mounted on a glass fiber. Single crystal diffraction data were collected at room temperature (293 K) on a Siemens Smart 1K CCD diffractometer with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation using the $\omega/2\theta$ scan mode at the temperature of 298 K. Lorentz and polarization corrections were applied to all data, and an empirical absorption correction was applied using SADABS program [18]. The space group was uniquely determined to be $P2_13$ (No. 198). Direct phase determination and subsequent Fourier syntheses using SHELXL-97 program [19] yielded the positions of all the atoms in the unit cell. To confirm the chemical composition was stoichiometric $K_2AlTi(PO_4)_3$, we do microprobe elemental analyses of a single crystal, indicating the presence of K, Al, Ti and P elements in a molar ratio of 8.08:4.24:4.13:13.68. Since sample is unpolished and X-ray corrections may be approximate, the EDS result is in agreement with those from single crystal X-ray structural analyses (2:1:1:3). In the initial least-square refinement, the occupancy factors of two K sites were set freely. The results show that they were close to 1.0 and were therefore fixed at 1.00 in the following refinement. The Al and Ti atoms are in substitutional type disorder, so the atomic position and anisotropic displacement parameters of Al and Ti were therefore constrained to be identical at each Al|Ti site, while the sum site occupancy was set at 1.00 for the langbeinite framework [12,14]. For the two Al|Ti sites are special position, the corresponding *sof* instructions of Al1, Ti1, Al2 and Ti2 atoms were set as 20.33333, –20.33333, 30.33333 and –30.33333, while two free variables were set to refine the occupancy factors of them. Moreover, to consistent with the EDS results and to achieve electroneutrality, a SUMP instruction was used to restraint Al and Ti atoms were in molar ratio of 1:1. The final structure refinement performed by least-square methods with atomic coordinates and anisotropic thermal parameters resulted in the satisfactory residuals of $S = 1.038$, $R_1 = 0.0313$ and $\omega R_2 = 0.0813$, for observed data ($I > 2\sigma(I)$). Final difference Fourier maps were essentially featureless with residual peaks of 0.568 and –1.247 e Å^{–3}. The crystallographic data collection and refinement parameters are summarized in Table 1. The atomic coordinates, site occupancies, selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $K_2AlTi(PO_4)_3$.

Atom	Site	<i>sof</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
K1	4a	1	0.81959(18)	0.18041(18)	0.68041(18)	0.0319(7)
K2	4a	1	0.96065(19)	0.46065(19)	0.03935(19)	0.0283(7)
Ti1	4a	0.566(14)	0.89043(12)	0.60957(12)	0.39043(12)	0.0031(6)
Al1	4a	0.434(14)	0.89043(12)	0.60957(12)	0.39043(12)	0.0031(6)
Ti2	4a	0.434(14)	0.66347(12)	0.16347(12)	0.33653(12)	0.0025(6)
Al2	4a	0.566(14)	0.66347(12)	0.16347(12)	0.33653(12)	0.0025(6)
P1	12b	1	0.97681(15)	0.29420(14)	0.37669(15)	0.0073(4)
O1	12b	1	0.8286(4)	0.2495(4)	0.3967(5)	0.0123(9)
O2	12b	1	0.8296(4)	0.5163(4)	0.5554(4)	0.0122(9)
O3	12b	1	1.0552(5)	0.2730(4)	0.5106(4)	0.0142(10)
O4	12b	1	1.0489(4)	0.2050(5)	0.2686(4)	0.0128(9)

^a *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 1
Crystal data and structure refinements for $K_2AlTi(PO_4)_3$.

Formula	$K_2AlTi(PO_4)_3$
Formula weight	437.96
Wavelength (Å)	0.71073
Crystal system	Cubic
Space group	$P2_13$
Unit cell dimensions	$a = 9.76410(10)$ Å
Volume, <i>Z</i>	4
<i>D</i> _{cal} (g cm ^{–3})	3.125
Absorption correction	Empirical
Absorption coefficient (mm ^{–1})	2.469
<i>F</i> (0 0 0)	892
Crystal size (mm)	0.150 × 0.050 × 0.050
θ range(deg)	2.95–25.61
Limiting indices	(–11, –11, –11) to (10, 7, 11)
<i>R</i> _{int}	0.0301
Reflections collected	5203
Independent reflections	597
Parameter/restraints/date (obs)	61/1/591
GOF on <i>F</i> ²	1.042
Final <i>R</i> indices [$I > 2\sigma(I)$]	<i>R</i> ₁ = 0.0299 <i>R</i> ₂ = 0.0987
<i>R</i> indices (all date)	<i>R</i> ₁ = 0.0305 <i>R</i> ₂ = 0.0995
Largest difference peak and hole (e Å ^{–3})	0.568 and –1.247

$$R_1 = \sum ||F_{obs}| - |F_{calc}|| / \sum |F_{obs}|, wR_2 = \left[\sum w(F_{obs}^2 - F_{calc}^2)^2 / \sum w(F_{obs}^2) \right]^{1/2}.$$

2.4. Computational descriptions

The crystallographic data of $K_2AlTi(PO_4)_3$ determined by X-ray was used for the theoretical calculations. Band structure calculations along with density of states (DOS) were carried out with density functional theory (DFT) using one of the non-local gradient-corrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code [20–22], which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons [23]. The number of plane waves included in the basis is determined by a cutoff energy of 450 eV and the numerical integration of the Brillouin zone is performed using a 2 × 2 × 2 Monkhorst-Pack k-point sampling. The interactions between the ionic cores and the electrons are described by the norm-conserving pseudopotential, in which the orbital electrons of K-3s²3p⁶4s¹, Al-3s²3p¹, Ti-3d²4s², P-3s²3p³ and O-2s²2p⁴ are treated as valence electrons.

3. Results and discussion

3.1. Crystal structure

Compound $K_2AlTi(PO_4)_3$ is isostructural to langbeinite [K₂Mg₂(SO₄)₃] and crystallize in the cubic space group $P2_13$. Its crystal structure features a three-dimensional anionic network of [AlTi(PO₄)₃]^{2–} interconnected by K⁺ cations (Fig. 2). Alternatively it can be described as the cations (K⁺, Al³⁺ and Ti⁴⁺) surrounded by isolated anions ([PO₄]^{3–}) (Fig. 3). In this structure, it was not

Table 3
Selected bond distances (Å) and angles (°) for $K_2AlTi(PO_4)_3$.

K1—O1	2.852(5) × 3	Ti1/Al1—O4	1.905(4) × 3
K1—O4	2.913(5) × 3	Ti1/Al1—O2	1.943(5) × 3
K1—O3	2.977(5) × 3	Al2/Ti2—O1	1.911(4) × 3
K1—O3	3.217(5) × 3	Al2/Ti2—O3	1.931(4) × 3
K2—O2	2.848(5) × 3	P1—O1	1.524(4)
K2—O4	3.036(5) × 3	P1—O3	1.529(5)
K2—O3	3.093(5) × 3	P1—O4	1.539(4)
K2—O4	3.462(4) × 3	P1—O2	1.540(4)
O4—Ti1/Al1—O4	90.4(2) × 3	O1—Al2/Ti2—O1	91.4(2) × 3
O4—Ti1/Al1—O2	178.56(19) × 3	O1—Al2/Ti2—O3	172.59(19) × 3
O4—Ti1/Al1—O2	88.56(18) × 3	O1—Al2/Ti2—O3	84.31(19) × 3
O4—Ti1/Al1—O2	90.60(18) × 3	O1—Al2/Ti2—O3	94.75(18) × 3
O2—Ti1/Al1—O2	90.44(18) × 3	O3—Al2/Ti2—O3	90.1(2) × 3
O1—P1—O3	109.1(3)	O1—P1—O2 ^{vii}	110.7(2)
O1—P1—O4	111.1(2)	O3—P1—O2 ^{vii}	111.2(2)
O3—P1—O4	106.3(3)	O4—P1—O2 ^{vii}	108.4(2)

possible to separate Al^{3+} and Ti^{4+} at the respective octahedron site. The atomic position and anisotropic displacement parameters of Al^{3+} and Ti^{4+} were therefore constrained to be identical, and the Al/Ti disorder with a relative occupancy of 1/1.

The asymmetric unit of $K_2AlTi(PO_4)_3$ contains two potassium(III) atoms, two Al/Ti mixed sites, one phosphorus and four oxygen atoms. The phosphorus(V) atom is four coordinated by four oxygen atoms, forming isolated $[PO_4]^{3-}$ anions. The $[PO_4]^{3-}$ has a tetragonal structure, in which the P^{5+} is located at the center of the tetragonal structure with four O^{2-} located at the four apex angles forming PO_4 tetrahedron. The P—O distances fall in the range of 1.524(4)–1.539(4) Å, and O—P—O bond angles range from 106.3(3) to 111.2(2)°, which are comparable to those reported in other metal phosphates [4]. Results of bond valence calculations indicate that the phosphorus atom is in +5 oxidation state. K(1) and K(2) atoms are 12-coordinated by twelve phosphate oxygens. The K(1)—O distances are in the range of 2.852(5)–3.217(5) Å, whereas the K(2)—O distances are of 2.848(5)–3.413(2) Å. It should be noted that there are three weak K—O contacts in 12 K—O contacts (i.e. K(1)—O(3) with 3.217(5) Å × 3 and K2—O4 with 3.462(4) Å × 3), which can be considered as secondary coordination bonds. Al(1)/Ti(1) and Al(2)/Ti(2) are coordinated by six oxygen atoms, forming distorted $X(1)O_6$ and

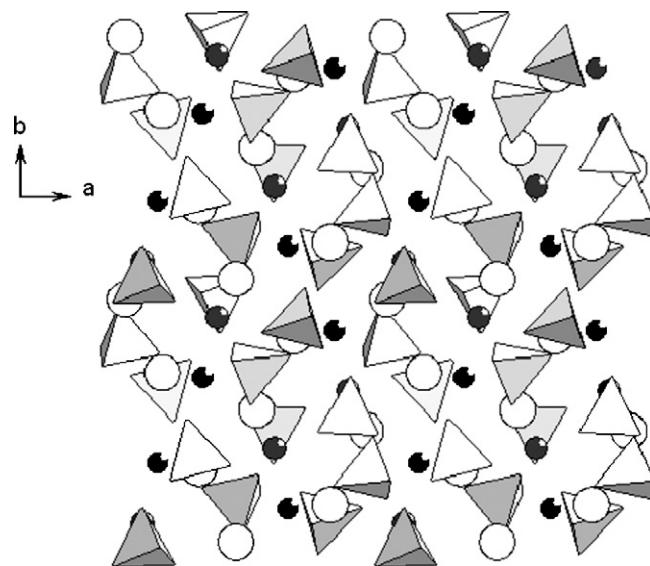


Fig. 3. View of the crystal structure of $K_2AlTi(PO_4)_3$ down the c -axis. K atoms are drawn as colorless circles; X (X=Al, Ti) atoms are drawn as dark circles; PO_4 polyhedra are shaded in medium dark gray.

$X(2)O_6$ (X=Al, Ti) octahedron. It should be noted that the occupancy of Ti atom in X(1) site (0.566) is slightly larger than in X(2) site (0.434). Generally, TiO_6 octahedron usually exhibits larger distortion than AlO_6 octahedron, so the fact of the different distortion between the X(1) site octahedron and X(2) site octahedron can be explained. As listed in Table 3, the bond lengths of X(1)—O are in the range of 1.905(4)–1.943(5) Å, whereas the X(2)—O distances are of 1.911(4)–1.931(4) Å.

Isolated $[PO_4]^{3-}$ anions are bridged by X^{n+} ($n=3$ for Al, 4 for Ti) cations into a $[AlTi(PO_4)_3]^{2-}$ 3D anionic network. In this network, XO_6 (X=Al, Ti) octahedron is coordinated by six PO_4 tetrahedron via corner-sharing O atoms, whereas each PO_4 tetrahedron is surrounded by four XO_6 octahedron. In view of topology, interconnected PO_4 and XO_6 (X=Al, Ti) polyhedra form three types of interconnected rings, as shown in Fig. 4. The rings include X—P—X—P four-number ring, X—P—X—P—X—P six-number ring and

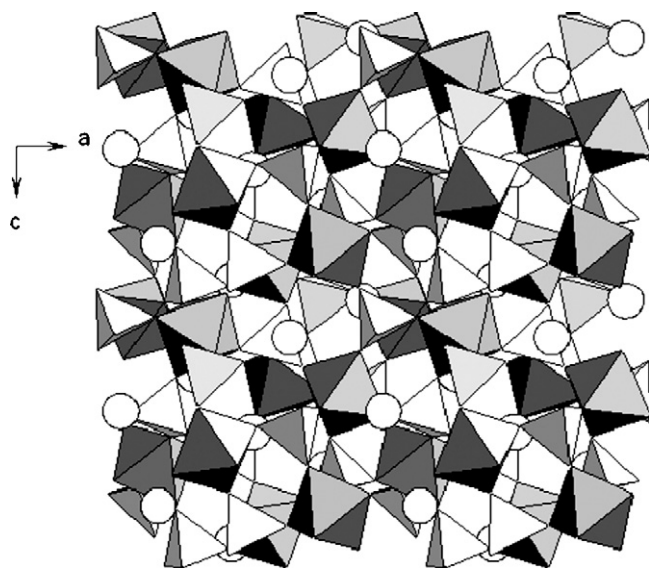


Fig. 2. View of the crystal structure of $K_2AlTi(PO_4)_3$ down the b -axis. K atoms are drawn as colorless circles; PO_4 and XO_6 (X=Al, Ti) polyhedra are shaded in medium and dark gray, respectively.

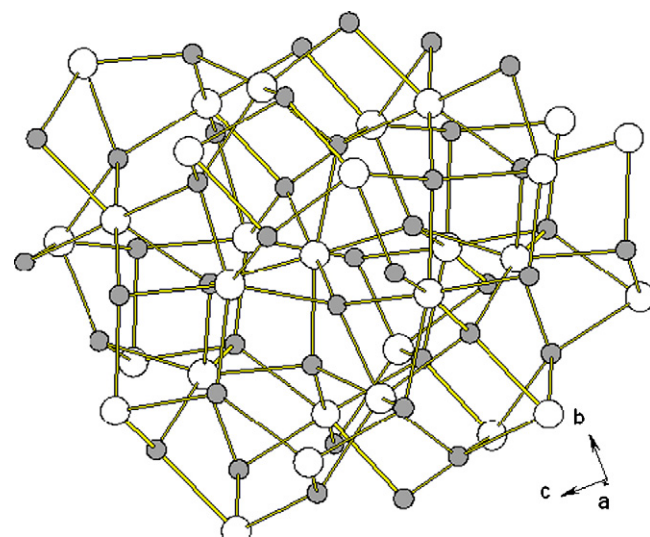


Fig. 4. View of the 3D $[AlTi(PO_4)_3]^{2-}$ anionic network. The X (X=Al, Ti) and P atoms are drawn as colorless and medium gray circles, respectively. O atoms are omitted for clarity.

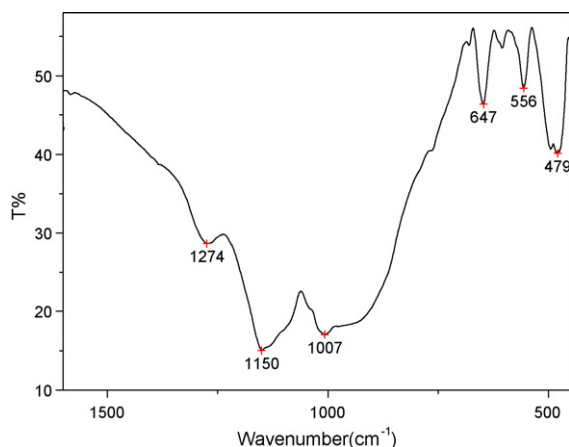


Fig. 5. The IR spectrum of $K_2AlTi(PO_4)_3$.

X–P–X–P–X–P–X–P eight-number ring. The resultant framework can be described as a 4,6-connected 3D net in which the vertex symbols (Schläfli notation) are 4^66^9 for six-connected X(1)O₆ groups, $4^66^68^3$ for six-connected X(2)O₆ groups and 4^36^3 for four-connected PO₄ groups.

The K⁺ cations reside among these $[AlTi(PO_4)_3]^{2-}$ anions and join them through coulombic action of K⁺ cations and O²⁻ anions to form 3D framework of $K_2AlTi(PO_4)_3$.

3.2. Optical properties

The IR spectrum of the compound $K_2AlTi(PO_4)_3$ is shown in Fig. 5. To assign the IR peaks to vibrational modes, we examine the modes and frequencies observed in similar compounds. The broad and intense absorption bands appearing at 1274, 1150, 1007 cm^{−1} are characteristic of P–O stretching vibration in the PO₄ tetrahedron, band group at 650–550 cm^{−1} is bending vibrations of P–O bond, and band at 479 cm^{−1} is due to X–O (X = Al, Ti) vibration. The UV-vis absorption spectrum of $K_2AlTi(PO_4)_3$ was determined by diffuse reflection measurement. As shown in Fig. 6, the strong absorption peak appears at around 220 nm.

3.3. Theoretical studies

The calculated band structure of $K_2AlTi(PO_4)_3$ along high symmetry points of the first Brillouin zone is plotted in Fig. 7, where the labeled k-points are present as X (0.5, 0.0, 0.0), R (0.5, 0.5, 0.5),

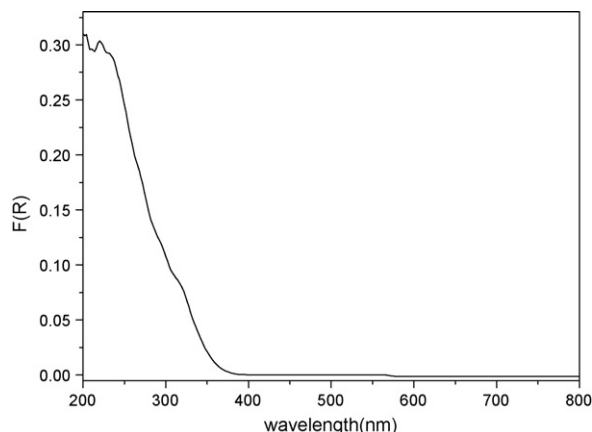


Fig. 6. The absorption spectrum of $K_2AlTi(PO_4)_3$.

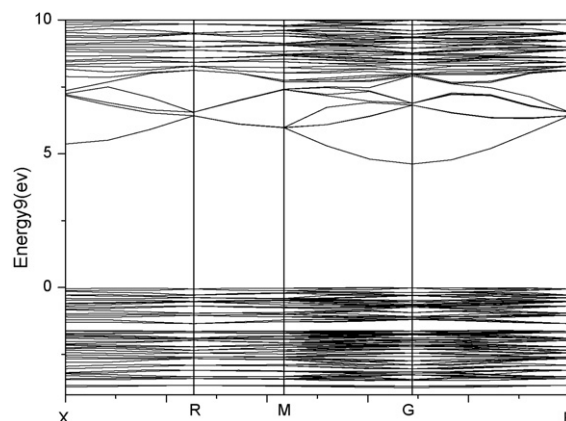


Fig. 7. Calculated energy band structure of $K_2AlTi(PO_4)_3$ in the range from −4.0 to 10.0 eV. The Fermi level is set at 0.0 eV.

Table 4

The state energies (eV) of the lowest conduction band (L–CB) and the highest valence band (H–VB) at some k-points of the crystal $K_2AlTi(PO_4)_3$.

k-Point	X	R	M	G
L–CB	5.365	6.419	5.977	4.618
H–VB	−0.034	−0.049	−0.022	−0.015

M (0.5, 0.5, 0.0) and G (0.0, 0.0, 0.0). It is observed that the top of valence bands (VBs) appears to be flat and the bottom of conduction bands (CBs) has dispersion observed along X–R–M–G–R. The state energies (eV) of the lowest conduction band (L–CB) and the highest valence band (H–VB) at some k-points of the crystal $K_2AlTi(PO_4)_3$ are listed in Table 4. The lowest energy (4.62 eV) of conduction bands (CBs) localized at G point, whereas the highest energy (0.00 eV) of valence bands (VBs) is also localized at G point. Hence, $K_2AlTi(PO_4)_3$ is an insulator with a direct band gap of 4.62 eV.

The bands can be assigned according to total and partial densities of states (DOS), as plotted in Fig. 8. The regions below the Fermi level (the Fermi level is set at the top of the valence band) contain 192 bands (4 formula units/unit cell) and can be divided into four regions. The states of K-3s form the VBs lying near −27.2 eV. The VBs ranging from −20.5 to −16.6 eV are composed of the states of Al-3s3p, Ti-4s3d, P-3s3p and O-2s states. The VBs near −11.2 eV are mainly composed of K-3p states. The fourth region of the VBs between −9.20 eV and the Fermi level (0.0 eV) is dominated by the O-2p, mixing with small amount of K-3s3p, Al-3s3p, Ti-4s3d, P-3s3p

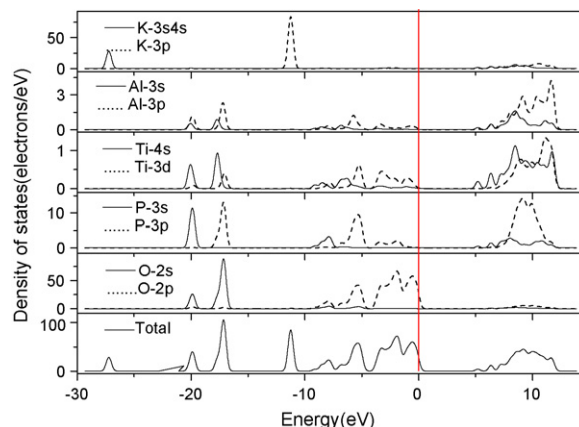


Fig. 8. Total and partial DOS of $K_2AlTi(PO_4)_3$.

and O-2s states. The CBs in the range of 4.6 and 6.5 eV are mostly contributions from P-3s, K-4s, Al-3s and Ti-4s, and the edge of CB is main the contribution from Ti-4s orbital. Accordingly, the peak of the absorption spectrum that is observed at 220 nm (5.65 eV) is assigned as the electron transitions between O-2p and Ti-4s states.

4. Conclusions

In the present work, the single-crystal structure of the stoichiometric compound $K_2AlTi(PO_4)_3$ synthesized by high temperature solid-state reactions has been determined and it crystallizes in cubic system with space group $P2_13$. It is observed that the UV-vis absorption peak is at about 220 nm, which mainly originates from O-2p to Ti-4s states. The calculated band structures show that the solid-state compound of $K_2AlTi(PO_4)_3$ is an insulator with a direct band gap of 4.62 eV.

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