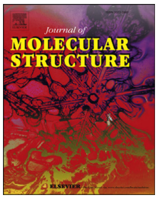
Journal of Molecular Structure 1151 (2018) 223–229

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



$Pb_{10}V_6O_{25}$: A new lead vanadate with apatite structure

Zhizhong Zhang [a], Xiaoyu Dong [b], Zhaohui Chen [a, *], Yunjing Shi [b], Qun Jing [a, **]

[a] College of Chemistry and Chemical Engineering, School of Physics and Technology, Xinjiang University, 666 Shengli Road, Urumqi 830046, China
[b] Engineering Department of Chemistry and Environment, Xinjiang Institute of Engineering, 236 Nanchang Road, Urumqi 830091, China

ARTICLE INFO

Article history:
Received 22 August 2017
Received in revised form
12 September 2017
Accepted 13 September 2017
Available online 18 September 2017

Keywords:
$Pb_{10}V_6O_{25}$
Crystal structure
Optical properties
Theoretical calculation

ABSTRACT

The apatite-type crystal $Pb_{10}V_6O_{25}$ has been grown from high temperature solution by spontaneous crystallization. It crystallizes in the hexagonal space group $P6_3/m$ with lattice parameters $a = 10.1045(6)$ Å, $c = 7.3503(6)$ Å and $Z = 1$. The structure of $Pb_{10}V_6O_{25}$ is composed of $Pb(1)O_9$ polyhedra and VO_4 tetrahedra, which form infinite $Pb(1)V_6O_{24}$ three-dimension (3D) framework with hexagonal star tunnels along the *c* axis, where $Pb(2)_3O(4)$ groups are filled. The band gap for $Pb_{10}V_6O_{25}$ is calculated to be 2.86 eV, from the UV–Vis–NIR diffuse reflectance spectrum. First-principles calculations are performed to elucidate the electronic structure and optical properties. Thermal behavior and vibration spectroscopy of $Pb_{10}V_6O_{25}$ are also reported in this work.

1. Introduction

Vanadium-containing compounds have been investigated for a variety of applications, including as magnetic materials [1–4], catalysts [5–8], cathode materials [9–12], ion-exchange materials [13,14] birefringent materials [15,16], and nonlinear-optical materials [17–19]etc. The diverse applications attribute to the origination of various coordination environments and oxidation states found in vanadates. In general, vanadium may exist as V^0 (metallic), V^{2+}, V^{3+}, V^{4+} and V^{5+} depending on the synthesis procedure and chemical environment [20]. Therefore, it can form tetrahedron, pentahedron, triangular pyramids, and octahedron, and has many interesting properties [21].

In recent years, researchers have synthesized a series of vanadium oxide-based compounds with apatite structures, such as $A_5(VO_4)_3F$ (A = Ca, Sr, Ba) [22–24], $A_5(VO_4)_3Cl$ (A = Ca, Sr, Ba) [25,26], $Pb_5(VO_4)_3Cl$ [27]and $Ca_5(VO_4)_3OH$ [28]. Apatites are important materials with applications in medical prostheses, environmental remediation and catalysis [29–34]. In the aspect of optical applications, their robust physical properties coupled with various coordination environments have made them suitable vanadate hosts for optically characteristics [35,36].

In order to further investigate the crystal structures with physical properties, we have extended the study on the synthesis of vanadium-containing compounds with apatite structure. Single crystal of the title compound is obtained firstly during our attempt to explore new compounds in the Pb–V–O system. In this paper, the synthesis, crystal structure, vibrational spectroscopy, UV–Vis–NIR diffuse reflectance spectrum and theoretical calculations of the title compound are reported.

2. Experimental section

2.1. Synthesis

Polycrystalline samples of $Pb_{10}V_6O_{25}$ were synthesized by solid-state reaction method. A stoichiometric mixture of PbO (99.5%, Shanghai Shanpu Chemical Co., Ltd), and V_2O_5 (99.5%, Shanghai Shanpu Chemical Co., Ltd) was thoroughly ground and put into a corundum crucible. The sample was first preheated at 300 °C for 10 h and then heated at 500 °C for 24 h. Afterwards it was sintered at 600 °C and kept at this temperature for 72 h with several intermediate mixings and grindings, the pure $Pb_{10}V_6O_{25}$ were obtained.

2.2. Powder X-ray diffraction

The powder X-ray diffraction (XRD) data were collected at room temperature in the angular range of $2\theta = 10–70°$ with a step width of 0.02 and a fixed counting time of 1 s/step using an automated Bruker D2 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).

---

* Corresponding author.
** Corresponding author.
E-mail addresses: chenzhaohui@xju.edu.cn (Z. Chen), qunjing@xju.edu.cn (Q. Jing).

http://dx.doi.org/10.1016/j.molstruc.2017.09.036
0022-2860/

Fig. 1 shows the observed powder XRD patterns of $Pb_{10}V_6O_{25}$ together with those calculated from the single crystal data for comparison. It is clear that the observed XRD patterns are in good agreement with the theoretical ones, confirming the pure powder of this compound.

2.3. Single crystal growth

Single crystals of $Pb_{10}V_6O_{25}$ were grown by the spontaneous crystallization method. They were grown from a mixture of PbF_2 (17.164 g, 70 mmol), V_2O_5 (3.1829 g, 17.5 mmol) and NH_4HF_2 (3.9928 g, 5 mmol). The mixture of the raw materials was put in a platinum crucible, and the crucible was gradually heated to 600 °C and kept for 20 h to ensure that the solution mixed homogeneously, then it was crystallized spontaneously in the crucible mouth. When the crystal growth is completed, and followed by cooling to 500 °C at the rate of 2 °C/h. Finally, the temperature was cooled to room temperature at a rate of 10 °C/h. Needle-shaped yellow crystals are obtained (Fig. 2).

2.4. Single crystal X-ray diffraction

A single crystal of $Pb_{10}V_6O_{25}$ with dimensions 0.23 mm × 0.10 mm × 0.08 mm was selected under microscope, and then glued on the end of a glass fiber for single crystal X-ray determination study. The diffraction data were collected at room temperature on a Bruker Smart APEX II single crystal diffractometer equipped with a 4K CCD-detector (graphite Mo Kα radiation, $\lambda = 0.71073$ Å). The reduction of data were carried out with the Bruker Suite software package [37]. The numerical absorption corrections were performed with the SADABS program and integrated with the SAINT program [38]. All calculations were performed with programs from the SHELXTL crystallographic software package [39]. The structures were solved by direct methods, and all of the atoms were refined using full-matrix least-squares techniques with anisotropic thermal parameters and finally converged for $F_o^2 \geq 2\sigma(F_o^2)$. The structures were examined using the Adsym subroutine of PLATON [40], and no additional symmetry could be applied to the models. Crystallographic data and structural refinements for the title compound are summarized in Table 1. The final refined atomic positions and isotropic thermal parameters of each atom are summarized in Table S1. Selected bond distances and angles are given in Table S2 in the Supporting Information.

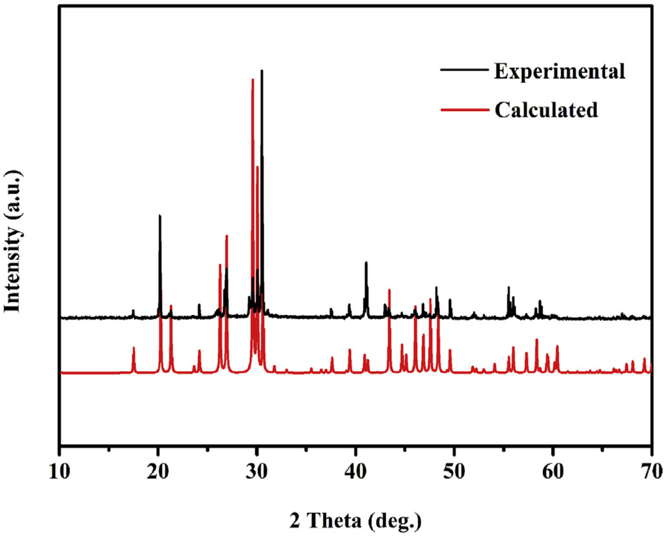


Fig. 1. Experimental and calculated XRD patterns of $Pb_{10}V_6O_{25}$.

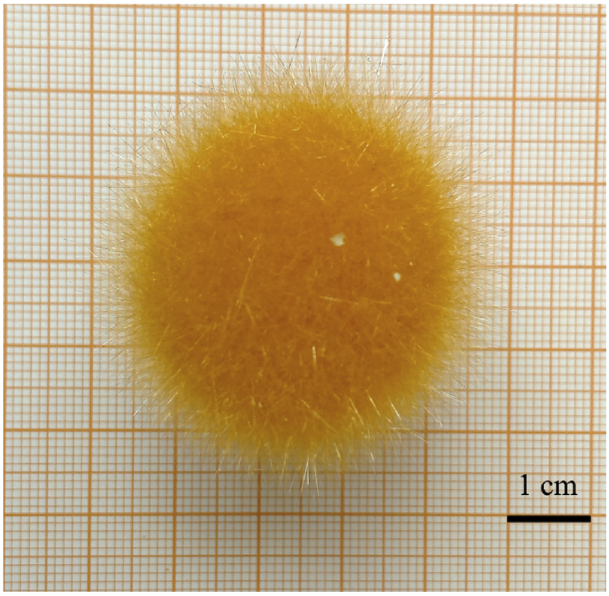


Fig. 2. Photograph of the $Pb_{10}V_6O_{25}$ crystals.

Table 1
Crystal data and structure refinement for $Pb_{10}V_6O_{25}$.

Empirical formula	$Pb_{10}V_6O_{25}$
Formula weight	2777.54
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system, space group	hexagonal, $P6_3/m$
Unit cell dimensions	$a = 10.1045(6)$ Å $b = 10.1045(6)$ Å $c = 7.3503(6)$ Å $\gamma = 120°$
Volume	649.93(8) Å^3
Z, Calculated density	1, 7.097 mg/m^3
Absorption coefficient	66.625 mm^{-1}
F(000)	1158
Crystal size	0.23 mm × 0.10 mm × 0.08 mm
Theta range for data collection	4.03–25.05°
Limiting indices	$-12 \leq h \leq 12$, $-12 \leq k \leq 10$, $-8 \leq l \leq 8$
Reflections collected/unique	4127/416 [R(int) = 0.1246]
Completeness to theta = 25.05	99.50%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	416/6/41
Goodness-of-fit on F^2	1.141
Final R indices [I > 2sigma(I)][a]	$R_1 = 0.0481$, $wR_2 = 0.1294$
R indices (all data)[a]	$R_1 = 0.0491$, $wR_2 = 0.1303$
Extinction coefficient	0.0131(15)
Largest diff. peak and hole	5.559 and −2.798 e/Å^3

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

2.5. Energy-dispersive spectroscopy

Elemental analysis was performed on the single crystals using a HITACHI SU8010 scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) capabilities. The crystals were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 1 min. As a qualitative measure, EDS confirmed the presence of each reported element in the title compound.

2.6. Thermal analyses

Thermogravimetric analysis (TGA) and differential scanning