A cesium copper vanadyl-diphosphate: Synthesis, crystal structure and physical properties

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ABSTRACT

A non-centrosymmetric orthorhombic diphosphate, $Cs_2Cu_{1+x}(VO)_{2-x}(P_2O_7)_2$ ($x=0.1$) with $a=13.7364$ (2) Å, $b=9.2666(2)$ Å, $c=11.5678(2)$ Å, $Z=4$, has been isolated. Its 3D framework is built from Cu atoms in square pyramidal and square planar coordination, VO_5 tetragonal pyramids and P_2O_7 diphosphate groups, sharing vertices. Large channels are fulfilled by cesium atoms. The ESR study reveals a similarity in behaviour of two paramagnetic (Cu and V) subsystems. The temperature dependences of the ESR linewidth and static magnetic susceptibility data present evidences for a cluster type magnetic ordering in the title compound at $T^*=22$ K. The weakness of the relevant anomalies reflects presumably obvious Cu^{2+} ions and $(VO)^{2+}$ units disorder in the system. It is supposed that the charge and geometry of the framework are controlled by the $Cu^{2+}/(VO)^{2+}$ ratio; its variation may lead to a design of new materials.
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1. Introduction

Vanadyl-phosphates have been a subject of interest for many decades because of their potential application as catalysts, ion conductors and sorbents. Representatives of this family with V^{4+} belong to the low-dimensional magnetic systems and can exhibit different types of magnetic ordering. Numerous vanadyl-diphosphates, namely $M_2VOP_2O_7$ (M=Ag, Li, Rb, Cs, Na [1–5]), $M(VO)_3(P_2O_7)_2$ (M=K, Sr, Pb, Ba [6–7]), $M_2(VO)_3(P_2O_7)_2$ (M=Cs, Rb, K [8–9]), $BaV_2P_2O_{10}$ [10] and $M_2VO(P_2O_7)_2$ (M=V, Fe, Cr) [11] are known to be obtained in the system M–V(IV)–P–O. Their crystal structures are based on 2D or 3D mixed anionic frameworks formed from diphosphate groups and vanadium tetragonal pyramids and/or octahedra, sharing oxygen vertices. Currently, rather limited number of phosphate crystal structures simultaneously containing copper(II) and vanadium(IV) atoms has been investigated, i.e. $CuV_2O_2(PO_4)_2$ [12], $Rb_2Cu(VO_2)_2(PO_4)$ [2,13], $CaCu(VO)(PO_4)_2$ and $CaCu_{1.13}(VO)_{0.87}(PO_4)_2$ [14]. Two latter compounds were synthesized by solid state reactions and differ mainly by chemical ratio of copper and vanadium cations. Their crystal structures built particularly of planar CuO_4-squares and VO_{1+4} pyramids are characterized by

isomorphous $Cu^{2+} \leftrightarrow VO^{2+}$ substitution. The phenomenon of Cu^{2+} replacement for V^{4+} is well known in cuprates, high-Tc superconductors [15,16].

Most of the above-mentioned vanadyl(IV)-phosphates were synthesized by solid-state and flux methods under vacuum. Our exploration of the system Cs–V–Cu–P–O in the air led to the synthesis of a first complex copper vanadium diphosphate with acentric novel type crystal structure reported here.
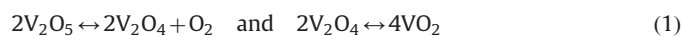
2. Experimental section

2.1. Synthesis and chemical composition

Single crystals of $Cs_2Cu_{1+x}(VO)_{2-x}(P_2O_7)_2$ ($x=0.1$) were obtained by spontaneous crystallization from the melt in the system Cs–Cu–V–P–O. The starting agents were CsH_2PO_4, CuO and V_2O_5 taken in a molar ratio of 2:2:1. The reaction mixture was placed in the Al_2O_3 crucible and heated to 850 °C, isothermed for 72 h and finally cooled to room temperature. Two phases obtained in a course of this experiment were mechanically extracted from a yellow transparent glass. The new compound was presented by green-bluish columnar crystals up to $0.1 \times 0.3 \times 1.0$ mm of an amount estimated of 65% of the total yield. The second phase ($\sim$10%) was identified as transparent colorless isometric crystals

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of α-$Cu_2P_2O_7$ [17]. The presence of V^{4+} in the sample obtained may be explained by the fact that above 700 °C V_2O_5 dissociates into V_2O_4 and O_2 [18] according to the following equations:

$$2V_2O_5 \leftrightarrow 2V_2O_4 + O_2 \quad \text{and} \quad 2V_2O_4 \leftrightarrow 4VO_2 \tag{1}$$

Thus, under the experimental condition we used, vanadium is likely to stay as V^{4+}.

Very small crystals of the title compound (as a minor phase) were also found in previous experiments of solid state reaction in the same system at 700 °C. A semi-quantitative X-ray spectral analysis (Leo 1429VP, energy-dispersive diffraction spectrometer INCA 350) of the phase showed the presence of Cs, Cu, V, P, and O atoms with an atomic ratio of Cu:V equal to 1.06:1.93 (result of 4 analyses) that is close to the ratio established by X-ray structural investigation.

2.2. Raman microspectroscopy

The Raman spectrum of a single crystal of the title compound was recorded using a confocal XPloRA Raman microscope (Horiba Jobin–Yvon) in the range of 300–3000 cm^{-1} with the exciting laser beam with wavelength of 532 nm. Each spectrum was accumulated in multi windows accumulation mode with 2×20 s exposure. Acquisition parameters (2400T grating, 300 μm hole, 100 μm slit, $100 \times$ objective) provide laser spot size of ~ 1 μm and spectral resolution of ~ 3 cm^{-1}.

2.3. X-ray analysis

The crystal structure of the title compound is found by single-crystal X-ray diffraction methods. The determination of unit cell parameters and data collection for the full Ewald sphere, were performed on a four-circle Xcalibur-S diffractometer equipped with CCD detector, using MoKα ($\lambda = 0.71073$ Å) radiation (graphite mono-chromator) at 298 K. The intensities were integrated and corrected for Lorentz and polarization effects. A numerical absorption correction was applied. Table 1 reports the crystallographic characteristics of the our phase and the experimental conditions of data collection and refinement. Atomic scattering curves and anomalous dispersion corrections were taken from the "International Tables for Crystallography" [19]. The crystal structure was solved via direct methods and refined against the F2 data using SHELX programs [20] in the framework of a Wingx32 software package [21].

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD427933.

2.4. Magnetic and resonance measurements

Magnetic properties of $Cs_2Cu_{1+x}(VO)_{2-x}(P_2O_7)_2$, (where $x = 0.1$) were measured by vibrating sample magnetometer (VSM) of Physical Properties Measurement System "Quantum Design" PPMS—9T in 2–300 K. Powder samples were obtained by crushing single crystals of the title compound in an agate mortar. Electron spin resonance (ESR) studies were carried out using an X-band ESR spectrometer CMS 8400 (ADANI) ($f \approx 9.4$ GHz, $B \leq 0.7$ T) equipped with a low temperature mount, operating in the range $T = 8$–300 K. The effective g-factor has been calculated with respect to a BDPA (a,g -bisdiphenyline-b-phenylallyl) reference sample with get = 2.00359.

3. Results and discussions

3.1. Raman spectra

The interpretation of Raman spectra was made on the basis of characteristic vibrations of P_2O_7 group and vanadium polyhedra in comparison with structurally related vanadyl-diphosphates. In the Raman spectrum shown in Fig. 1, there are a number of strong bands assigned to the vibrations of P_2O_7 groups. The most intense

Table 1
Crystallographic data, experimental details and results of structure refinement.

Crystal data	
Formula, M(g/mol)	$Cs_2Cu_{1.1}(VO)_{1.9}(P_2O_7)_2$, 810.79
Crystal system, space group	Orthorhombic, $Pn2_1a$ (No. 33)
a, b, c (Å)	13.7364(2), 9.2666(2), 11.5678(2)
V (Å^3), Z	1472.46(5), 4
D_c (g/cm^3)	3.657
Crystal size (mm^3)	$0.09 \times 0.10 \times 0.35$
Crystal color	Green-bluish
Absorbtion coefficient μ (mm^{-1})	8.148
Data collection	
Diffractometer	Xcalibur-S-CCD
Radiation, λ (Å)	MoKα, 0.71073, graphite monochromator
Temperature (K)	293(2)
Scan mode	ω
Reflections collected	31196
R_{int}, R_{σ}	0.0516, 0.0296
θ_{max} (°)	30.0
h, k, l range	$-19 \leq h \leq 19, -13 \leq k \leq 13, -16 \leq l \leq 16$
Refinement	
Program used to refine	SHELXL
Refinement method	Least-squares calculation on F^2
Independent/observed reflections [$I > 2\sigma(I)$]	4292/3780
Number of refined parameters	239
Correction for absorption	On the crystal shape
T_{max}, T_{min}	0.561, 0.246
Weighting scheme	$1/[s^2(Fo^2) + (0.0228P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$
R value [$F_{obs} > 4\sigma(F_{obs})$]	$R1 = 0.0295$, w$R_2 = 0.0600$
R value (all data)	$R1 = 0.0361$, w$R_2 = 0.0630$
GOF	1.068
Largest diff peak, hole/e (Å^{-3})	0.838, -0.741
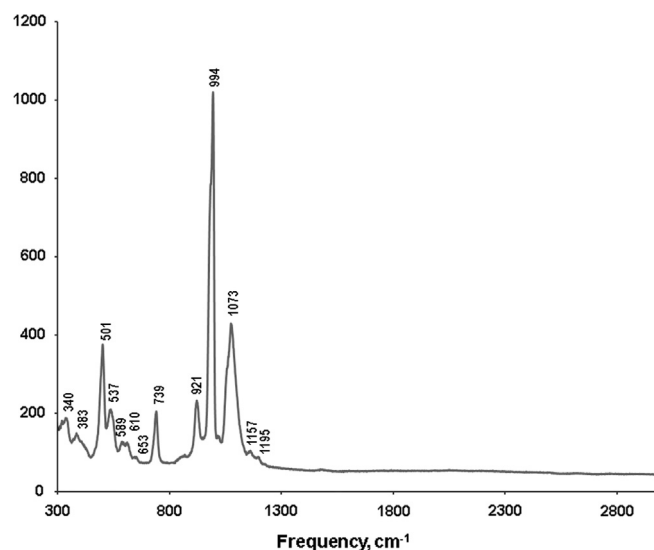
Fig. 1. Raman spectra of $Cs_2Cu_{1+x}(VO)_{2-x}(P_2O_7)_2$.