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Synthesis and Crystal Structure Analysis of $KAg_{11}(VO_4)_4$

Anton Kovalevskiy and Martin Jansen

Stuttgart, Max-Planck-Institut für Festkörperforschung

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Abstract. New potassium silver vanadate $KAg_{11}(VO_4)_4$ was obtained by reacting the stoichiometric mixture of Ag_2O and V_2O_5 at elevated oxygen pressure, adding a small portion of aqueous KOH. The synthesis was done at 573 K and 430 MPa of oxygen pressure. The crystal structure was solved by direct methods basing on single crystal diffraction data (*P*bca, Z = 4, a = 16.533(1), b = 10.6286(7), c = 10.5452(7) Å, 3983 independent reflections, R_1 = 5.4 %). The optical band gap for $KAg_{11}(VO_4)_4$ was determined as 2.0 eV. According to magnetic measurements, $KAg_{11}(VO_4)_4$ is diamagnetic.

Keywords: Potassium silver vanadate; Elevated oxygen pressure; Crystal structure

Introduction

In a systematic approach we continue to explore ternary silver oxide systems by reacting mixtures of the constituent binary oxides, applying elevated oxygen pressures [1−11]. During these studies we have noticed that adding small portions of aqueous KOH frequently enhances reactivity and promotes crystal growth. Surprisingly, the more basic KOH, as compared to Ag_2O, was not included in the products, at least in not detectable amounts [5−8]. However, applying this procedure at investigating the Ag_2O/V_2O_5 system we obtained a potassium silver vanadate(V), $KAg_{11}(VO_4)_4$, containing stoichiometric amounts of potassium. The synthesis and structural characterization of $KAg_{11}(VO_4)_4$ are discussed below.

Experimental Part

Reacting a mixture of Ag_2O and V_2O_5 (molar ratio 2.75:1), to which a small portion of aqueous KOH was added, at elevated oxygen pressure, has yielded $KAg_{11}(VO_4)_4$ as a coarse crystalline, brilliant red product.

Table 1 Most intensive observed powder reflections for $KAg_{11}(VO_4)_4$ (d > 1.5 Å, I > 1 %). Results of a profile fit using the positional parameters from the single crystal investigation (Tab. 2−4).

Nr.	h	k	l	d / Å	I / %	Nr.	h	k	l	d / Å	I / %
1	2	0	0	8.2667	1.8	23	1	5	1	2.0675	3.9
2	1	1	1	6.8197	13.9	24	8	0	0	2.0667	12.2
3	2	2	0	4.4704	1.7	25	1	1	5	2.0528	3.4
4	4	0	0	4.1334	2.7	26	5	3	3	1.9919	3.2
5	0	2	2	3.7431	2.0	27	3	3	4	1.9746	1.8
6	3	3	1	2.8679	2.8	28	3	5	1	1.9492	1.1
7	3	1	3	2.8548	3.5	29	3	1	5	1.9368	1.2
8	4	2	2	2.7745	100.0	30	4	4	3	1.8862	1.2
9	5	1	2	2.7089	2.4	31	0	4	4	1.8715	12.9
10	0	4	0	2.6572	17.4	32	8	2	2	1.8092	1.4
11	0	0	4	2.6364	17.2	33	1	3	5	1.8015	1.2
12	3	3	2	2.5945	1.1	34	6	4	2	1.7981	1.2
13	0	4	1	2.5767	1.2	35	5	1	5	1.7538	1.6
14	1	3	3	2.4674	4.4	36	3	1	6	1.6541	1.7
15	6	0	2	2.4422	2.5	37	8	4	0	1.6314	10.5
16	2	4	2	2.2808	1.1	38	8	0	4	1.6265	10.1
17	3	3	3	2.2732	7.9	39	4	6	1	1.6092	1.3
18	2	2	4	2.2709	1.8	40	7	5	1	1.5626	4.7
19	7	1	1	2.2525	2.4	41	7	1	5	1.5562	3.6
20	6	2	2	2.2191	1.2	42	4	6	2	1.5558	13.7
21	0	4	3	2.1197	1.1	43	4	2	6	1.5474	11.1
22	1	3	4	2.0980	1.4						

The starting silver and vanadium oxides were obtained by adding aqueous KOH to a $AgNO_3$ (Sigma-Aldrich 99+ %) aqueous solution, and decomposition of solid NH_4VO_3 (Sigma-Aldrich 99+ %) under oxygen flow at 300 °C, respectively. The mixture was annealed for 10 hours in gold crucibles, placed in a stainless-steel autoclave [12], at 573 K and 430 MPa of oxygen pressure and post washed with distilled water. Following this experimental procedure a mixture of $KAg_{11}(VO_4)_4$ and Ag_2O was obtained because soluble potassium vanadates formed simultaneously as a by-product, thus fixing a part of the vanadium oxide. Therefore, in order to obtain single phase $KAg_{11}(VO_4)_4$ an excess of vanadium oxide was used at the same temperature and oxygen pressure conditions (the 2:1 Ag:V molar ratio was used instead of 2.75:1, corresponding to the empirical formula) to compensate for the formation of soluble potassium vanadates which stay dissolved in the aqueous solution. If despite of this procedure, the row product contained the silver oxide admixture, it was removed by post washing with dilute aqueous acetic acid. The as obtained final product consists of coarse red $KAg_{11}(VO_4)_4$ crystals, which are insensitive to air and light.

X-ray investigations on powder samples were performed using the Stoe StadiP diffractometer supplied with a position sensitive detector and a curved germanium monochromator with Cu-$K_{\alpha1}$ radiation (λ = 1.54056 Å), at room temperature. The powder diffraction

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* Prof. Dr. Martin Jansen
Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
D-70569 Stuttgart
Fax: +49-711-6891502
E-mail: M.Jansen@fkf.mpg.de

Table 2 X-ray and crystallographic data[a)] for $KAg_{11}(VO_4)_4$.

Crystal data	
Empirical formula	$KAg_{11}V_4O_{16}$
Formula weight / g mol^{-1}	1685.4
Crystal system	orthorhombic
Space group, Z	*P*bca (No. 61), 4
Lattice constants (from powder)	
a / Å	16.533(1)
b / Å	10.6286(7)
c / Å	10.5452(7)
V / Å^3	1853.0(2)
Calculated density / g cm^{-3}	6.041
Crystal shape, color	compact, red transparent
Crystal size / mm	0.1 x 0.1 x 0.1
Data collection	
Diffractometer	Bruker AXS Smart-CCD
Monochromator	Graphite
Wavelength / Å	0.71073
Temperature / K	293
2Θ range for data collection	2Θ < 70.1
hkl-range	$-26 \le h \le 25$, $-16 \le k \le 16$, $-16 \le l \le 16$
Total no. reflection	36995
Unique reflections	3983
Unique reflections with $I > 2\sigma(I)$	3685
Absorption coefficient / mm^{-1}	13.54
F(000)	3024
Structure refinement	
Structure solution, refinement	ShelXL'97
Parameters refined	149
R_1 $I > 2\sigma(I)$, all data	0.0500, 0.0540
wR_2 $I > 2\sigma(I)$, all data	0.1033, 0.1052
ΔF_{max}, ΔF_{min} / e Å^{-3}	1.25, −1.75
Extinction coefficient	0.00070(4)

[a)] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-391344, the name of authors, and citation of the paper.

Table 3 Atomic coordinates and isotropic thermal displacement parameters (U_{eq})[a)] for $KAg_{11}(VO_4)_4$.

Atom	Site	x	y	z	U_{eq} (in Å^2)
Ag1	*8c*	0.13298(3)	0.22291(4)	0.51847(4)	0.0254(1)
Ag2	*8c*	0.13204(3)	0.78619(4)	0.47373(4)	0.0257(1)
Ag3	*8c*	0.12597(3)	0.99027(4)	0.28506(4)	0.0252(1)
Ag4	*8c*	0.12335(3)	0.02192(4)	0.71563(4)	0.0266(1)
Ag5	*8c*	0.25382(3)	0.24531(5)	0.74492(4)	0.0334(1)
Ag6	*4b*	0	0	1/2	0.0259(1)
V1	*8c*	0.26841(5)	0.01345(8)	0.50124(8)	0.0162(2)
V2	*8c*	0.99897(5)	0.26367(8)	0.75947(8)	0.0172(2)
K1	*4a*	0	0	0	0.0307(4)
O1	*8c*	0.9998(2)	0.3164(4)	0.9164(4)	0.0245(8)
O2	*8c*	0.2136(2)	0.1089(4)	0.3960(4)	0.0223(7)
O3	*8c*	0.9971(2)	0.1023(4)	0.7564(5)	0.0233(7)
O4	*8c*	0.9154(3)	0.3221(4)	0.6846(4)	0.0351(11)
O5	*8c*	0.3196(3)	0.1091(4)	0.6040(4)	0.0281(9)
O6	*8c*	0.2055(2)	0.9156(4)	0.5892(4)	0.0244(8)
O7	*8c*	0.0844(3)	0.3164(4)	0.6850(5)	0.0371(12)
O8	*8c*	0.3326(3)	0.9210(4)	0.4187(4)	0.0316(10)

[a)] $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$

data were collected in the range of 5 to 80 degrees in 2Θ. Experimental *d* values and relative intensities are given in Table 1. The profile refinement was performed using the JANA2000 program package [13]. The single crystal diffraction data were collected on a Bruker AXS Smart-CCD diffractometer (Mo-Kα radiation, graphite monochromator). The structure was solved by direct methods and refined using full-matrix least-squares techniques [14]. The final refinement included anisotropic displacement parameters for all atoms. See Table 2 for crystallographic data.

Table 4 Anisotropic thermal displacement parameters[a)] (in Å^2) for $KAg_{11}(VO_4)_4$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag1	0.0277(2)	0.02152(18)	0.0269(2)	0.00190(14)	0.00638(15)	−0.00069(14)
Ag2	0.0282(2)	0.02288(19)	0.0261(2)	0.00027(15)	−0.00575(15)	−0.00137(15)
Ag3	0.0283(2)	0.02193(18)	0.0252(2)	−0.00160(14)	−0.00517(15)	−0.00045(14)
Ag4	0.0300(2)	0.0255(2)	0.0244(2)	0.00353(15)	0.00696(16)	0.00143(15)
Ag5	0.0441(3)	0.0301(2)	0.0261(2)	0.0033(2)	0.00256(19)	−0.00477(16)
Ag6	0.0252(3)	0.0293(3)	0.0233(3)	0.0007(2)	0.0003(2)	0.0065(2)
V1	0.0153(3)	0.0153(3)	0.0180(3)	−0.0002(3)	0.0008(3)	0.0005(3)
V2	0.0220(4)	0.0146(3)	0.0150(3)	−0.0010(3)	0.0000(3)	−0.0011(3)
K1	0.0339(9)	0.0381(10)	0.0202(7)	−0.0040(7)	0.0024(7)	−0.0002(7)
O1	0.0227(17)	0.033(2)	0.0179(17)	0.0005(15)	−0.0011(14)	−0.0061(15)
O2	0.0221(17)	0.0234(17)	0.0215(17)	0.0040(14)	−0.0035(14)	−0.0017(14)
O3	0.0206(16)	0.0177(15)	0.032(2)	0.0011(13)	−0.0010(15)	−0.0001(15)
O4	0.051(3)	0.025(2)	0.029(2)	0.0129(19)	−0.021(2)	−0.0083(17)
O5	0.031(2)	0.0283(19)	0.0254(19)	−0.0077(16)	−0.0121(16)	0.0058(16)
O6	0.0241(18)	0.0250(18)	0.0242(18)	−0.0055(14)	0.0052(15)	−0.0034(15)
O7	0.049(3)	0.030(2)	0.033(2)	−0.017(2)	0.022(2)	−0.0135(18)
O8	0.032(2)	0.032(2)	0.031(2)	0.0129(18)	0.0154(18)	0.0110(18)

[a)] The anisotropic displacement factors exponent takes the form:
$-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{13} + 2a^*b^*hkU_{12})$

Magnetic measurements were performed on a SQUID-Magnetometer (MPMS 5.5, Quantum Design) between 5 and 300 K in magnetic fields 0.1 and 1 T. A diffuse reflectance spectrum was recorded on a Perkin Elmer Lambda 9 UV/VIS/NIR Spectrophotometer.

Results and Discussion

$KAg_{11}(VO_4)_4$ has been obtained by the solid state reaction at elevated oxygen pressure [12] as a coarse crystalline red product. Experimental X-ray powder diffraction patterns (Tab. 1), which could be indexed orthorhombic with the refined lattice constants a = 16.533(1) Å, b = 10.6286(7) Å, c = 10.5452(7) Å, have shown, that the sample was single phase; also, the measured pattern agrees perfectly with the calculated one.

The crystal structure of the new potassium silver vanadate was determined from single crystal data collected at 293 K. For details of the structure refinement and crystallographic data see Tab. 2-4. For interatomic distances, coordination numbers (CN), effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR) [15] see Tab. 5.

Table 5 Interatomic distances (in Å), coordination numbers (CN), effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR, in Å) [15] for $KAg_{11}(VO_4)_4$.

Atom	O1	O2	O3	O4	O5	O6	O7	O8	CN	ECoN	MEFIR
Ag1	2.486	2.216					2.172	2.421	4	3.4	0.80
Ag2	2.489			2.174	2.464	2.202			4	3.3	0.80
Ag3		2.249	2.301		2.361		2.410		4	3.9	0.88
Ag4			2.299	2.456		2.211		2.341	4	3.8	0.84
Ag5		2.320		2.890	2.342	2.535	2.969	2.920	6	3.4	0.95
Ag6	2.141								2	2.0	0.74
	2.141										
V1		1.756			1.710	1.739		1.688	4	4.0	0.29
V2	1.747		1.716	1.708			1.710		4	4.0	0.31
K1	3.477		2.790	3.053	3.383		3.092	3.017	12	8.9	1.48
	3.477		2.790	3.053	3.383		3.092	3.017			
CN	5	4	4	5	5	4	5	5			
ECoN	3.6	4.0	4.0	3.8	4.1	3.8	3.8	3.9			
MEFIR	1.46	1.42	1.42	1.45	1.46	1.44	1.45	1.47			

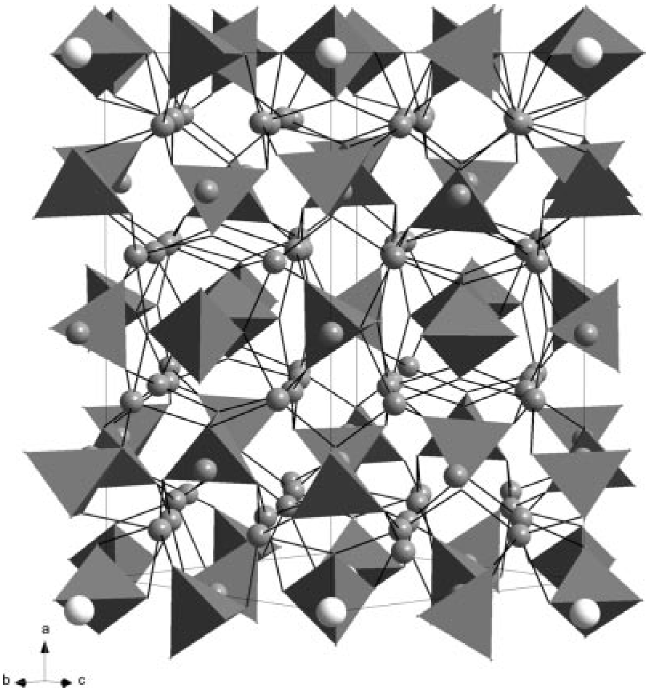

Fig 1 Crystal structure of $KAg_{11}(VO_4)_4$. Dark gray spheres represent silver atoms, white spheres represent potassium, vanadium oxide tetrahedra are gray.

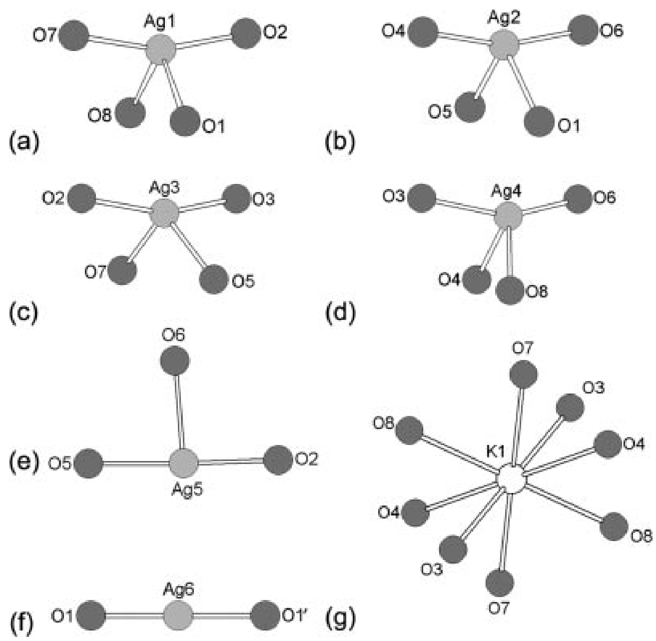

Fig. 2 Coordination environments of silver and potassium atoms in $KAg_{11}(VO_4)_4$. (a)−(d) Irregular sawing horse, Ag1−Ag4. (e) Three-fold planar, Ag5. (f) Two-fold coordinated, Ag6. (g) Distorted bi-capped trigonal antiprism, K1. Light gray spheres represent silver atoms, white sphere represents potassium atom, dark gray spheres represent oxygen atoms.

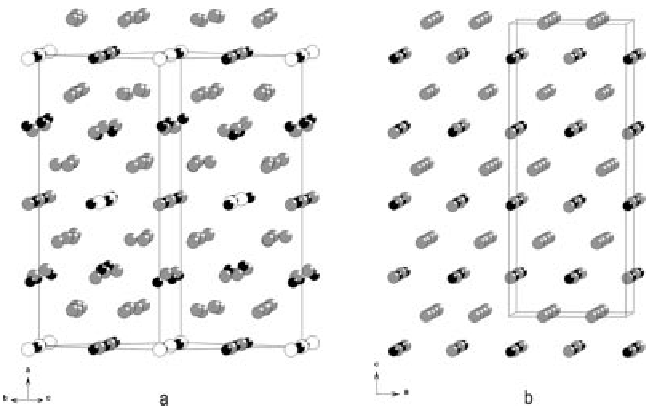

Fig. 3 Three-dimensional cation packing of $KAg_{11}(VO_4)_4$ (a, view along [0 1 1]) and of $Ag_6(SO_4)(SiO_4)$ [16] (b, view along [0 1 0]). Black spheres represent the tetrahedron-forming atoms (vanadium in case of $KAg_{11}(VO_4)_4$ and sulfur and silicon in case of $Ag_6(SO_4)(SiO_4)$). Silver atoms are gray, and potassium atoms are white. The oxygen atoms are not shown.

The crystal structure of $KAg_{11}(VO_4)_4$ is made up of isolated, fairly regular VO_4^{3-} tetrahedra based on two crystallographically unique vanadium atoms with 1.69 − 1.76 Å V−O bond lengths (Tab. 5) and O−V−O angels varying from 107° to 111°. The metallic ions sit in the pockets between the negatively charged vanadium oxide tetrahedra, which leads to irregular coordination environments. The different coordination environment around the cations creates six crystallographically independent silver sites and one potassium site (Fig. 1).

At a maximum coordination distance for silver atoms of 2.7 Å, Ag1, Ag2, Ag3 and Ag4 are four-coordinate, Ag5 is three-coordinate and Ag6 is two-coordinate. Both Ag1 and Ag2 are prevailingly two-fold linearly coordinated (by O2, O7, and O4, O6, respectively) with Ag−O distances varying from 2.174 Å to 2.216 Å, with two oxygen atoms (O1, O8, and O5, O1, respectively) in the second coordination sphere forming a sawing horse geometry. The other four-coordinated silver atoms, Ag3 and Ag4, are coordinated in irregular sawing horse geometry as well, but without a distinguished two-fold coordination. The Ag−O distances vary from 2.249 Å to 2.410 Å for Ag3, and from 2.211 Å to 2.456 Å for Ag4. The triangular planar coordination geometry of Ag5 is made up of O2, O5 and O6. It can be described as a two-fold linear coordination by O2 and O5, with O6 in the second coordination sphere. Ag6 is two-fold linearly coordinated by O1 × 2. The K1 coordination forms a distorted bi-capped trigonal antiprism geometry. The antiprism is made up of O3 × 2, O4 × 2 and O8 × 2 with two faces of the antiprism capped by O7. See Figure 2 and Table 5 for interatomic distances.

The cation partial structure of $KAg_{11}(VO_4)_4$ can be related to one in $Ag_6(SiO_4)(SO_4)$ [16, 17]. Following this analogy, the structure (see Fig. 3) may be described as alternate $[Ag_4]^{4+}$ and $[Ag_2(VO_4)_2]^{4-}$ layers, where in every second of the latter one half of silver atoms is substituted by potassium. The resulting stacking sequence is:

$$\{-[Ag_4]^{4+}-[Ag_2(VO_4)_2]^{4-}-[Ag_4]^{4+}-[KAg(VO_4)_2]^{4-}-\}$$

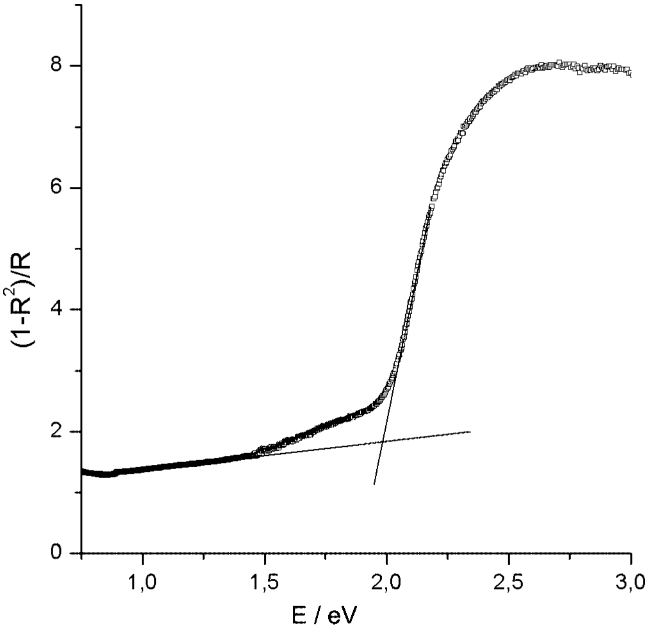

Fig. 4 Diffuse reflectance spectrum of $KAg_{11}(VO_4)_4$ (R-reflectance).

The accommodation of large potassium cations in the structure of $KAg_{11}(VO_4)_4$ causes a significant distortion of the cation partial structure, in comparison with the one found in $Ag_6(SiO_4)(SO_4)$.

Using the diffuse reflectance spectrum data (Fig. 4) the optical band gap for $KAg_{11}(VO_4)_4$ was determined as 2.0 eV, which is in good agreement with the red color of the crystals and the absorption data for other red ternary silver oxides [18]. Since VO_4^{3-} anions are colorless, the absorption band was attributed to Ag-Ag interactions [19]. According to the magnetic measurements, $KAg_{11}(VO_4)_4$ is diamagnetic.

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