



## Article

Special Issue dedicated to Peter Williams

# Relianceite-(K), a new phosphate–oxalate mineral related to davidbrownite-(NH<sub>4</sub>) from the Rowley mine, Arizona, USA

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### Abstract

Relianceite-(K),  $K_4Mg(V^{4+}O)_2(C_2O_4)(PO_3OH)_4(H_2O)_{10}$ , is a new mineral species from the Rowley mine, Maricopa County, Arizona, USA. It occurs in an unusual bat-guano-related, post-mining assemblage of phases. Other secondary minerals associated with relianceite-(K) are antipinite, dendorait-(NH<sub>4</sub>), fluorite, mimetite, mottramite, rowleyite, salammoniac, struvite, vanadinite, willemite, wulfenite and at least one other new mineral. Crystals of relianceite-(K) are sky blue prisms up to ~0.1 mm in length. The streak is very pale blue and lustre is vitreous, Mohs hardness is 2½, tenacity is brittle and fracture is splintery. The calculated density is 2.111 g·cm<sup>-3</sup>. Relianceite-(K) is optically biaxial (+) with  $\alpha = 1.528(2)$ ,  $\beta = 1.529(2)$ ,  $\gamma = 1.562(2)$  (white light);  $2V_{meas} = 22(1)^\circ$ ; orientation  $Z = \mathbf{b}$ ; pleochroism:  $X = \text{colourless}$ ,  $Y = \text{pale blue}$ ,  $Z = \text{pale blue}$ ;  $X < Y \approx Z$ . Electron microprobe analysis gave the empirical formula  $[K_{2.21}(NH_4)_{1.79}]_{\Sigma 4.00}Mg_{0.96}(V_{0.95}^{4+}O)_2(C_2O_4)[P_{1.03}O_{3.03}(OH)_{0.97}]_4(H_2O)_{10}$ , with the C, N and H contents constrained by the crystal structure. Raman spectroscopy confirmed the presence of NH<sub>4</sub> and C<sub>2</sub>O<sub>4</sub>. Relianceite-(K) is monoclinic,  $Pc$ , with  $a = 12.404(7)$  Å,  $b = 9.014(6)$ ,  $c = 13.260(8)$  Å,  $\beta = 100.803(10)^\circ$ ,  $V = 1456(2)$  Å<sup>3</sup> and  $Z = 2$ . The structural unit in the crystal structure of relianceite-(K) ( $R_1 = 0.0540$  for 3751  $I_o > 2\sigma I$  reflections) is a  $(V^{4+}O)_2(C_2O_4)(PO_3OH)_4$  chain in which VO<sub>6</sub> octahedra are bridged by an oxalate group to form  $[V_2C_2O_{12}]$  dimers, PO<sub>3</sub>OH tetrahedra form a double bridge between the VO<sub>6</sub> octahedra of the dimers, and additional PO<sub>3</sub>OH tetrahedra decorate the chain. Topologically, this is the same chain found in the structure of davidbrownite-(NH<sub>4</sub>). The MgO(H<sub>2</sub>O)<sub>5</sub> octahedron can be considered a distant decoration on the chain. The chains are linked to each other through an extensive system of K/NH<sub>4</sub>-O bonds and hydrogen bonds.

**Keywords:** relianceite-(K), new mineral species, phosphate, oxalate, crystal structure, davidbrownite-(NH<sub>4</sub>), Rowley mine, Arizona

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### Introduction

The still actively forming bat-guano assemblage in the Rowley mine in southwestern Arizona, USA, has proven to be a prolific source of new minerals. Including the new mineral described herein, relianceite-(K), eight new minerals have now been described from this assemblage. Relianceite-(K),  $K_4Mg(V^{4+}O)_2(C_2O_4)(PO_3OH)_4(H_2O)_{10}$ , is one of only five minerals known to include both phosphate and oxalate group, the others being davidbrownite-(NH<sub>4</sub>),  $(NH_4)_5K(V^{4+}O)_2(C_2O_4)[PO_{2.75}(OH)_{1.25}]_4 \cdot 3H_2O$  (Kampf *et al.*, 2019a), dendorait-(NH<sub>4</sub>),  $(NH_4)_2NaAl(C_2O_4)(PO_3OH)_2(H_2O)_2$  (Kampf *et al.*, 2022), phoxite,  $(NH_4)_2Mg_2(C_2O_4)(PO_3OH)_2(H_2O)_4$  (Kampf *et al.*, 2019b), and thebaite-(NH<sub>4</sub>),  $(NH_4)_3Al(C_2O_4)(PO_3OH)_2(H_2O)$  (Kampf *et al.*, 2021a); all of these,

except phoxite, are known only from the Rowley mine bat guano assemblage. One of these, dendorait-(NH<sub>4</sub>), is intimately associated with relianceite-(K) and is described in a companion paper (Kampf *et al.*, 2022).

In 1922, the Rowley Copper Mining Company was reorganised as the Reliance Copper Company in an effort to raise funds through stock offerings. Although the effort was unsuccessful and the newly formed Rowley Mines, Inc. took control of the mine in 1927, the mine was often referred to as the Reliance mine in subsequent years. The mineral name ‘relianceite’ is based upon this alternate name for the mine. For naming and species definition, the total combined occupancy of the four large cation sites in the structure is employed; thereby, the ‘-(K)’ suffix in the name reflects the fact that  $K^+ > NH_4^+$ . If an analogue with  $NH_4^+ > K^+$  were found, it would be named relianceite-(NH<sub>4</sub>).

The new mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2020-102, Kampf *et al.*, 2021b). The holotype specimen of relianceite-(K) is

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deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, USA, catalogue number 75275. This is also the holotype for dendoraite-(NH<sub>4</sub>).

### Occurrence

Relianceite-(K) was found on the 125-foot level of the Rowley mine, ~20 km NW of Theba (small settlement and railroad depot), Maricopa County, Arizona, USA (33°2'57"N 113°1'49.59"W). The Rowley mine is on the western slope of the Painted Rock Mountains (in the Painted Rock mining district) and overlooks the Dendora Valley, immediately to the west. It is a former Cu–Pb–Au–Ag–Mo–V–baryte–fluorspar mine that exploited veins presumed to be related to the intrusion of an andesite porphyry dyke into Tertiary volcanic rocks. Although the mine has not been operated for ore since 1923, collectors took notice of the mine as a source of fine wulfenite crystals around 1945. An up-to-date account of the history, geology, and mineralogy of the mine was published recently by Wilson (2020).

The new mineral was found in a hot and humid area of the mine (see figure 26 in Wilson, 2020) in an unusual bat guano-related, post-mining assemblage of phases that include a variety of vanadates, phosphates, oxalates and chlorides, some containing NH<sub>4</sub><sup>+</sup>. This secondary mineral assemblage is found growing on baryte–quartz-rich matrix and, besides relianceite-(K), includes allantoin (Kampf *et al.*, 2021c), ammineite, antipinite, apthitalite, bassanite, biphosphammite, cerussite, davidbrownite-(NH<sub>4</sub>) (Kampf *et al.*, 2019a), dendoraite-(NH<sub>4</sub>) (Kampf *et al.*, 2022), fluorite, halite, hydroglauberite, mimetite, mottramite, natrosulfatourea (Kampf *et al.*, 2021c), perite, phoxite (Kampf *et al.*, 2019b), rowleyite (Kampf *et al.*, 2017), salammoniac, struvite, thebaite-(NH<sub>4</sub>) (Kampf *et al.*, 2021a), thénardite, urea, vanadinite, weddellite, willemite, wulfenite, and several other potentially new minerals. Relianceite-(K) was found in intimate association with antipinite, dendoraite-(NH<sub>4</sub>), fluorite, mimetite, mottramite, rowleyite, salammoniac, struvite, vanadinite, willemite, wulfenite, and at least one other potentially new species.

### Physical and optical properties

Crystals of relianceite-(K) are sky blue prisms, up to ~0.1 mm in length, often forming radiating sprays (Fig. 1). The blades are elongate on [010] with shallow pyramidal terminations; the observed crystal forms are {100}, { $\bar{1}00$ }, {001} and {00 $\bar{1}$ }; although terminal forms could not be measured, the appearance of crystals suggests some combination of the forms {010}, {110}, { $\bar{1}10$ }, {011} and {01 $\bar{1}$ } (Fig. 2). No twinning was observed, but inversion twinning is inferred from structure refinement. The streak is very pale blue, the lustre is vitreous, the Mohs hardness is ~2½, the tenacity is brittle and the fracture is splintery. No cleavage could be observed with certainty because of the small crystal size; however, the structure suggests two cleavages in the [010] zone, probably perfect on {100} and good on {001}. The tiny crystals are virtually invisible in density liquids making the measurement of their density impossible. The calculated density is 2.111 g·cm<sup>-3</sup> using the empirical formula and 2.204 g·cm<sup>-3</sup> using the ideal (K-end-member) formula. Relianceite-(K) is non-fluorescent in long- and short-wave ultraviolet light. The mineral is insoluble at room temperature in H<sub>2</sub>O, but easily soluble in dilute HCl.

Relianceite-(K) is optically biaxial (+) with  $\alpha = 1.528(2)$ ,  $\beta = 1.529(2)$  and  $\gamma = 1.562(2)$  determined in white light. The 2V

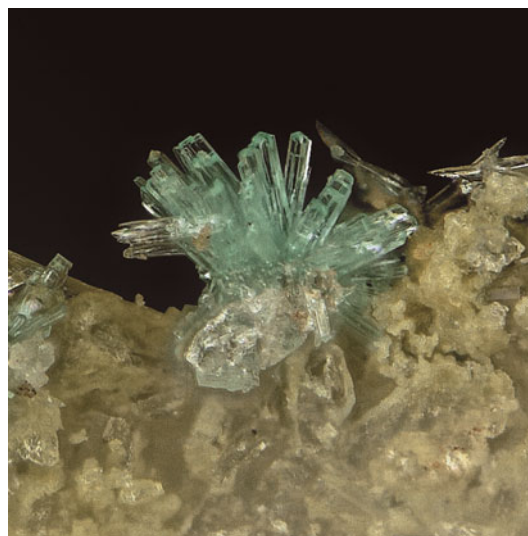


Fig. 1. Spray of relianceite-(K) prisms on the holotype specimen (#75275); field of view 0.3 mm across.

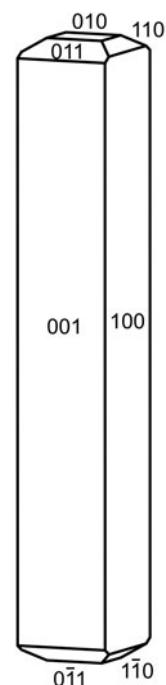


Fig. 2. Crystal drawing of relianceite-(K); clinographic projection in non-standard orientation, **b** vertical.

measured using extinction data with *EXCALIBUR* (Gunter *et al.*, 2004) is 22(1)°; the calculated 2V is 20.1°. The partially determined optical orientation is  $Z = \mathbf{b}$  (length slow). The mineral is pleochroic:  $X = \text{colourless}$ ,  $Y = \text{pale blue}$ ,  $Z = \text{pale blue}$ ; and  $X < Y \approx Z$ .

### Raman spectroscopy

Raman spectroscopy was conducted on a Horiba XploRA PLUS spectrometer using a 532 nm diode laser, 100  $\mu\text{m}$  slit and 1800 gr/mm diffraction grating and a 100 $\times$  (0.9 NA) objective.

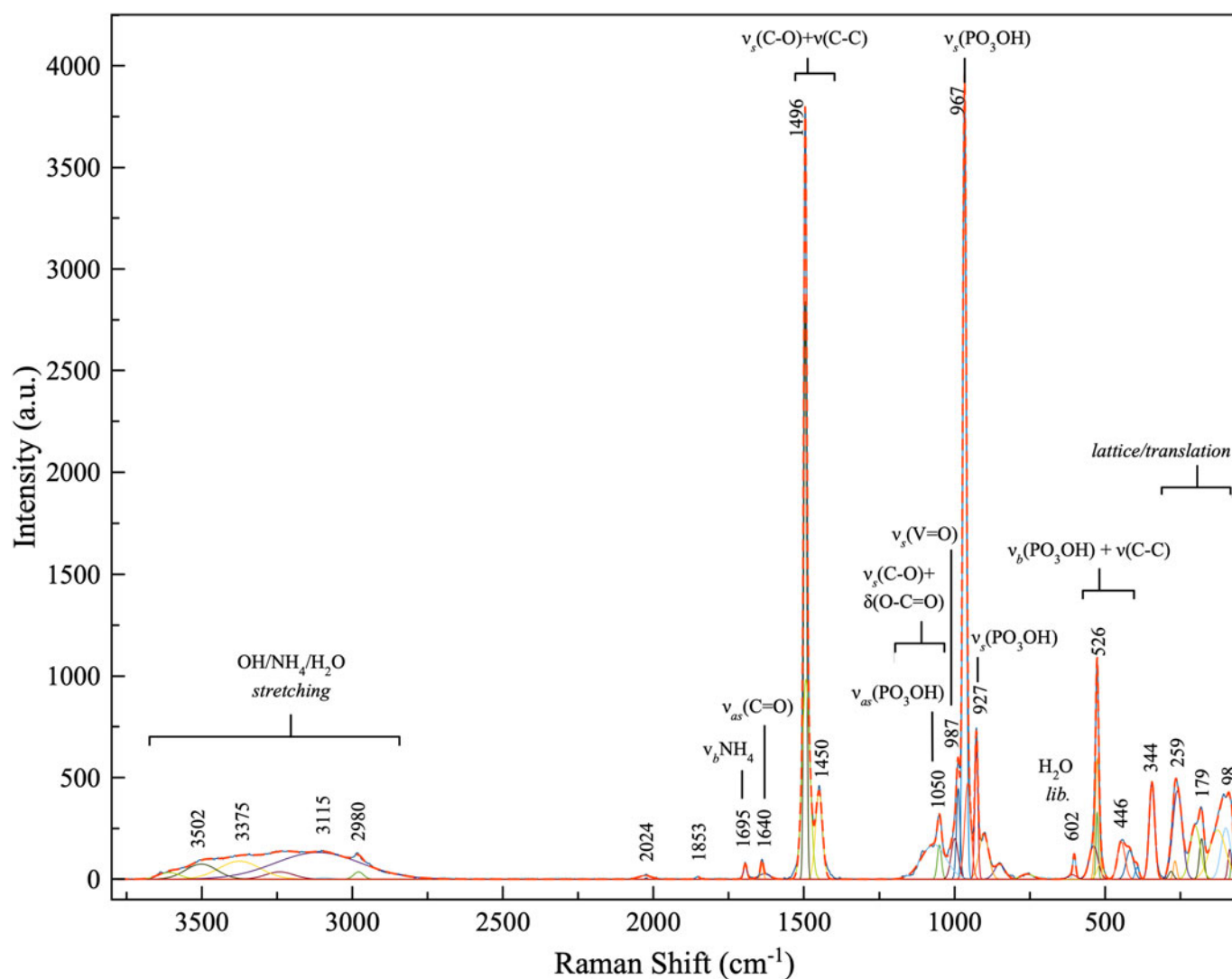


Fig. 3. Raman spectrum of relianceite-(K).

Full pattern peak fitting was performed using the least-squares approach using Gaussian peak shapes to minimise the difference between measured and calculated profiles, and cubic-spline was used for base-line modelling. The spectrum from 3800 to 60  $\text{cm}^{-1}$  is shown in Fig. 3 including labelled mode assignments based on several references: Frost (2004), Frost *et al.* (2011), Hardcastle and Wachs (1991), Kouvatas *et al.* (2017), Ma and He (2012), Mohaček-Grošev *et al.*, (2009), Rudolph and Irmer (2007), Sergeeva *et al.* (2019), Števkó *et al.* (2018) and Yakovenchuk *et al.* (2018).

### Chemical analysis

Analyses (6 points) were performed at Caltech on a JEOL 8200 electron microprobe in wavelength dispersive spectroscopy mode. Analytical conditions were 15 kV accelerating voltage, 5 nA beam current and 5  $\mu\text{m}$  beam diameter. During vacuum deposition of the conductive carbon coat required for electron probe microanalysis (EPMA), relianceite-(K) clearly suffered loss of much of the weakly held  $\text{H}_2\text{O}$  and probably a portion of its  $\text{NH}_4$ . Relianceite-(K) was very sensitive to the electron beam and additional loss of these components probably occurred

during the EPMA. The very large loss in  $\text{H}_2\text{O}$  resulted in much higher concentrations for the remaining constituents than are to be expected for the fully hydrated phase; therefore, the other analysed constituents have been normalised to provide a total of 100% when combined with the calculated  $\text{H}_2\text{O}$  content. To account for the loss of  $\text{NH}_4$ ,  $(\text{NH}_4)_2\text{O}$  was calculated so that  $\text{K} + \text{NH}_4 = 4$  atoms per formula unit (apfu) in accord with the structure. We attribute the large variation in analysed  $(\text{NH}_4)_2\text{O}$  content to analytical problems, rather than to actual compositional variation. Insufficient material is available for CHN analysis; however, the fully ordered structure and detailed bond-valence analysis unambiguously established the anion ( $\text{O}$ ,  $\text{OH}$ ,  $\text{H}_2\text{O}$  and  $\text{C}_2\text{O}_4$ ) identities and the corresponding quantitative contents of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Analytical data are given in Table 1.

The empirical formula (based on  $\text{P} + \text{V} = 6$  and  $\text{O} = 32$  apfu) is  $[\text{K}_{2.21}(\text{NH}_4)_{1.79}]_{\Sigma 4.00}\text{Mg}_{0.96}(\text{V}_{0.95}^{4+}\text{O})_2(\text{C}_2\text{O}_4)[\text{P}_{1.03}\text{O}_{3.03}(\text{OH})_{0.97}]_4(\text{H}_2\text{O})_{10}$ . The simplified formula is  $(\text{K},\text{NH}_4)_4\text{Mg}(\text{V}^{4+}\text{O})_2(\text{C}_2\text{O}_4)(\text{PO}_3\text{OH})_4(\text{H}_2\text{O})_{10}$  and the ideal (K-end-member) formula is  $\text{K}_4\text{Mg}(\text{V}^{4+}\text{O})_2(\text{C}_2\text{O}_4)(\text{PO}_3\text{OH})_4(\text{H}_2\text{O})_{10}$ , which requires  $\text{K}_2\text{O}$  19.49,  $\text{MgO}$  4.17,  $\text{VO}_2$  17.16,  $\text{P}_2\text{O}_5$  29.37,  $\text{C}_2\text{O}_3$  7.45,  $\text{H}_2\text{O}$  22.36, total 100 wt.%. The Gladstone-Dale compatibility

**Table 1.** Analytical data (wt.%) for relianceite-(K).

Constituent	Mean	Min.	Max.	S.D.	Probe standard	Normalised
(NH <sub>4</sub> ) <sub>2</sub> O*	4.22	2.80	6.29	1.44	BN	5.04
K <sub>2</sub> O	13.09	12.23	13.99	0.58	Microcline	11.24
MgO	4.87	4.62	5.23	0.22	Forsterite	4.18
VO <sub>2</sub>	19.73	19.46	20.54	0.40	V <sub>2</sub> O <sub>5</sub>	16.94
P <sub>2</sub> O <sub>5</sub>	36.68	35.23	37.54	0.94	Apatite	31.50
C <sub>2</sub> O <sub>3</sub> *						7.78
H <sub>2</sub> O*						23.32
Total						100.00

\* (NH<sub>4</sub>)<sub>2</sub>O, C<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O values in the Normalised column are based on the structure. S.D. – standard deviation.

**Table 2.** Powder X-ray data (*d* in Å) for relianceite-(K)\*.

<i>l</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>l</i> <sub>calc</sub>	<i>hkl</i>	<i>l</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>l</i> <sub>calc</sub>	<i>hkl</i>
<b>100</b>	<b>12.22</b>	12.1842	100	1 0 0	<b>19</b>	<b>3.039</b>	3.0336	2	$\bar{3}$ 2 1
		9.0140	3	0 1 0			3.0261	10	2 2 2
13	7.34	7.4121	3	0 1 1			3.0171	1	3 2 0
		7.2465	8	1 1 0			3.0058	2	3 1 2
<b>21</b>	<b>6.56</b>	6.6555	5	$\bar{1}$ 1 1			2.9531	1	$\bar{2}$ 1 4
		6.5125	15	0 0 2			2.9348	1	1 2 3
<b>20</b>	<b>6.28</b>	6.2513	17	$\bar{1}$ 0 2	7	2.929	2.9294	5	$\bar{4}$ 1 1
15	6.07	6.0523	10	1 1 1			2.9173	2	1 3 0
9	5.27	5.2789	4	0 1 2	<b>22</b>	<b>2.893</b>	2.8957	6	$\bar{3}$ 2 2
		5.1369	3	$\bar{1}$ 1 2			2.8857	2	4 1 0
9	5.05	5.0474	2	2 1 0			2.8744	12	$\bar{1}$ 3 1
6	4.857	4.9738	3	$\bar{2}$ 1 1	14	2.844	2.8532	2	3 2 1
		4.9342	1	$\bar{2}$ 0 2			2.8311	7	$\bar{4}$ 1 2
11	4.613	4.5958	5	1 1 2			2.8199	1	1 3 1
6	4.366	4.3282	2	$\bar{2}$ 1 2			2.8106	2	$\bar{3}$ 0 4
7	4.245	4.2592	1	0 2 1			2.7283	1	0 3 2
		4.2271	3	1 2 0	<b>21</b>	<b>2.718</b>	2.7174	11	4 1 1
15	4.144	4.0997	5	$\bar{1}$ 2 1			2.6947	4	2 3 0
		4.0835	1	2 0 2			2.6834	1	$\bar{2}$ 3 1
18	3.935	3.9460	3	1 2 1			2.6712	1	2 0 4
		3.9221	4	$\bar{1}$ 1 3			2.6647	1	$\bar{1}$ 2 4
		3.9116	10	0 1 3			2.6394	1	0 2 4
		3.7335	2	$\bar{3}$ 1 1	9	2.632	2.6280	3	$\bar{4}$ 1 3
4	3.739	3.7196	3	2 1 2			2.6189	3	1 3 2
14	3.593	3.6232	3	2 2 0			2.6029	2	3 2 2
		3.5776	10	$\bar{2}$ 1 3			2.5965	1	2 3 1
		3.5538	1	1 1 3	4	2.579	2.5798	1	4 0 2
<b>19</b>	<b>3.435</b>	3.4850	6	$\bar{3}$ 1 2			2.5684	2	$\bar{2}$ 2 4
		3.4117	13	3 1 1			2.5528	1	$\bar{4}$ 2 1
		3.3944	1	2 2 1			2.5433	2	$\bar{1}$ 1 5
11	3.355	3.3277	3	$\bar{2}$ 2 2	10	2.509	2.5026	8	0 1 5
		3.3041	1	$\bar{1}$ 0 4			2.4769	1	$\bar{2}$ 1 5
		3.2563	1	0 0 4			2.4671	1	$\bar{4}$ 0 4
		3.1883	5	3 0 2	6	2.438	2.4368	2	5 0 0
<b>23</b>	<b>3.125</b>	3.1322	2	$\bar{1}$ 2 3	6	2.414	2.4239	2	$\bar{3}$ 3 1
		3.1268	7	0 2 3			2.4201	1	2 3 2
9	3.097	3.1023	13	$\bar{1}$ 1 4			2.4088	4	4 2 1
		3.0646	3	2 1 3	7	2.377	2.3849	1	$\bar{3}$ 2 4
		3.0460	1	4 0 0			2.3797	1	$\bar{2}$ 3 3
							2.3688	2	1 1 5

\*The strongest lines are given in bold.

(Mandarino, 2007)  $1 - (K_p/K_c)$  is  $-0.001$  in the range of superior compatibility for the empirical formula.

### X-ray crystallography and structure determination

Powder X-ray studies were done using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized MoK $\alpha$  radiation. A Gandolfi-like motion on the  $\varphi$  and  $\omega$  axes was

**Table 3.** Data collection and structure refinement details for relianceite-(K).

<b>Crystal data</b>	
Refined formula (H added)	[K <sub>2.84</sub> (NH <sub>4</sub> ) <sub>1.16</sub> ] <sub>Σ4</sub> Mg(V <sup>4+</sup> O) <sub>2</sub> (PO <sub>3</sub> OH) <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>10</sub>
Space group	<i>Pc</i>
Unit cell dimensions	<i>a</i> = 12.404(7) Å <i>b</i> = 9.014(6) Å <i>c</i> = 13.260(8) Å $\beta$ = 100.803(10)°
<i>V</i>	1456.3(15) Å <sup>3</sup>
<i>Z</i>	2
Density (calculated)	2.149 g·cm <sup>-3</sup>
Absorption coefficient	1.415 mm <sup>-1</sup>
F(000)	953.7
<b>Data collection</b>	
Diffractometer	Bruker D8 three-circle; multilayer optics; APEX-II CCD
X-ray radiation / source	MoK $\alpha$ ( $\lambda$ = 0.71073 Å) / rotating anode
Temperature (K)	293(2)
Crystal size ( $\mu$ m)	60 × 15 × 7
$\theta$ range for data collection	2.75 to 25.31°
Index ranges	$-14 \leq h \leq 14$ , $-10 \leq k \leq 10$ , $-15 \leq l \leq 15$
Reflections collected	9980
Independent reflections	5186 [ <i>R</i> <sub>int</sub> = 0.072]
Reflections with <i>I</i> <sub>o</sub> > 2 $\sigma$ <i>I</i>	3751
Completeness to $\theta$ = 25.31°	98.7%
<b>Refinement</b>	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Parameters / restraints	411 / 2
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.989
Final <i>R</i> indices [ <i>I</i> <sub>o</sub> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0540, <i>wR</i> <sub>2</sub> = 0.1236
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0865, <i>wR</i> <sub>2</sub> = 0.1392
Absolute structure parameter	0.44(8)
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$	0.54 and $-0.57$ e <sup>-</sup> /Å <sup>3</sup>

\**R*<sub>int</sub> =  $\sum |F_o^2 - F_c^2(\text{mean})| / \sum F_o^2$ . GoF =  $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$ . *R*<sub>1</sub> =  $\sum |F_o - |F_c|| / \sum F_o$ . *wR*<sub>2</sub> =  $\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where *a* is 0.0758, *b* is 0 and *P* is  $[2F_o^2 + \text{Max}(F_o^2, 0)]/3$ .

used to randomise the sample. Observed *d* values and intensities were derived by profile fitting using *JADE Pro* software (Materials Data, Inc., USA). The powder data are presented in Table 2. Unit-cell parameters refined from the powder data using *JADE Pro* with whole pattern fitting are *a* = 12.424(10), *b* = 9.030(10), *c* = 13.273(10) Å,  $\beta$  = 100.75(2)°, and *V* = 1463(2) Å<sup>3</sup>.

Single-crystal X-ray studies were done using a Bruker D8 three-circle diffractometer equipped with a rotating anode generator (MoK $\alpha$  X-radiation), multilayer optics and an APEX-II CCD area detector. Crystals of relianceite-(K) generally exhibit sub-parallel composite growth. The best crystal found after extensive searching still provided split diffraction spots. Using 40 s frames with a 0.3° frame width, a total of 34,188 reflections were integrated. The unit-cell dimensions were obtained by least-squares refinement of 4016 reflections with *I*<sub>o</sub> > 10 $\sigma$ *I*. Empirical absorption corrections (*SADABS*; Sheldrick, 2015) were applied and equivalent reflections were merged. Systematically absent reflections are consistent with the presence of a *c*-glide plane. The *E* statistics ( $|E^2 - 1| = 0.841$ ) did not provide an unambiguous choice between centrosymmetric and noncentrosymmetric space groups. The structure was subsequently solved in space group *Pc* by direct methods using *SHELXS-2013*. The structure was refined using *SHELXL-2016* (Sheldrick, 2015) and was modelled as an inversion twin. Four large-cation sites were refined with joint occupancies by K and N. Difference-Fourier syntheses failed to locate H atoms; however, detailed bond-valence assessment, including hydrogen-bond assignments, allowed O sites to be



**Table 4.** Atom positions, occupancy and displacement parameters ( $\text{\AA}^2$ ) for relicanteite-(K).

	Occupancy.	$x/a$	$y/b$	$z/c$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$	$U_{eq}$
V1	V	0.71959(18)	0.4759(3)	0.52070(17)	0.0230(14)	0.0205(15)	0.0138(15)	-0.0005(12)	0.0012(11)	-0.0021(11)	0.0194(6)
V2	V	0.90456(19)	0.0293(3)	0.65696(17)	0.0262(15)	0.0208(16)	0.0157(15)	0.0003(12)	0.0021(11)	0.0015(12)	0.0211(7)
Mg	Mg	0.2378(3)	0.3597(5)	0.6260(3)	0.025(2)	0.030(2)	0.021(2)	-0.0031(19)	-0.0009(17)	0.0007(18)	0.0259(10)
P1	P	0.0890(3)	0.2209(5)	0.2354(3)	0.0203(18)	0.022(2)	0.012(2)	0.0011(17)	0.0011(15)	-0.0015(16)	0.0181(9)
P2	P	0.6604(3)	0.1777(5)	0.6296(3)	0.022(2)	0.019(2)	0.020(2)	-0.0011(17)	0.0064(17)	-0.0005(17)	0.0200(10)
P3	P	0.5195(3)	0.2916(5)	0.9393(3)	0.0252(19)	0.020(2)	0.018(2)	-0.0008(17)	-0.0013(16)	-0.0028(17)	0.0217(9)
P4	P	0.9658(3)	0.3308(5)	0.5466(3)	0.0217(19)	0.017(2)	0.013(2)	0.0006(17)	0.0009(16)	0.0002(16)	0.0174(9)
K1	$K_{0.76}N_{0.24(2)}$	0.7495(4)	0.0882(5)	0.3801(3)	0.056(3)	0.030(3)	0.018(3)	0.001(2)	0.006(2)	0.007(2)	0.035(2)
K2	$K_{0.93}N_{0.07(2)}$	0.8637(3)	0.4179(5)	0.7941(3)	0.045(3)	0.041(3)	0.016(2)	-0.0001(18)	0.0027(17)	0.0017(19)	0.0347(17)
K3	$K_{0.65}N_{0.35(2)}$	0.5429(4)	0.4297(7)	0.2159(4)	0.047(4)	0.043(4)	0.035(4)	0.000(3)	0.013(3)	0.004(3)	0.041(2)
K4	$K_{0.50}N_{0.50(2)}$	0.0736(5)	0.0644(8)	0.9576(5)	0.049(5)	0.033(4)	0.027(4)	-0.003(3)	0.009(3)	-0.002(3)	0.036(3)
C1	C	0.8198(12)	0.2348(18)	0.0323(13)	0.022(8)	0.019(9)	0.023(9)	0.007(7)	0.002(7)	-0.003(7)	0.021(4)
C2	C	0.7961(11)	0.2526(19)	0.1409(12)	0.016(8)	0.030(10)	0.013(8)	-0.017(7)	0.000(6)	-0.003(7)	0.020(4)
O1	O	0.2037(8)	0.2574(12)	0.2241(9)	0.026(5)	0.036(6)	0.032(6)	0.004(5)	0.005(4)	-0.003(5)	0.032(3)
O2	O	0.0765(8)	0.1940(12)	0.3467(8)	0.036(6)	0.032(6)	0.011(6)	-0.001(5)	0.002(5)	-0.007(5)	0.027(3)
OH3	OH	0.0119(7)	0.3597(13)	0.1968(8)	0.024(5)	0.028(6)	0.035(6)	0.013(5)	0.008(4)	0.008(4)	0.029(2)
O4	O	0.0455(8)	0.0864(12)	0.1688(8)	0.027(6)	0.027(6)	0.018(6)	-0.005(5)	0.003(5)	-0.006(5)	0.024(3)
O5	O	0.7573(8)	0.1069(11)	0.5935(8)	0.021(5)	0.024(7)	0.027(6)	0.002(5)	0.009(5)	-0.002(5)	0.023(3)
O6	O	0.6557(8)	0.3452(13)	0.6148(8)	0.031(6)	0.026(6)	0.027(6)	-0.001(5)	0.008(4)	-0.007(5)	0.028(3)
O7	O	0.5539(9)	0.1086(14)	0.5804(12)	0.018(6)	0.040(7)	0.094(11)	-0.034(7)	0.013(6)	-0.017(5)	0.050(4)
OH8	OH	0.6766(10)	0.1540(16)	0.7490(9)	0.060(8)	0.048(8)	0.020(7)	0.011(6)	0.019(6)	0.023(7)	0.041(3)
O9	O	0.5748(8)	0.4217(13)	0.0052(9)	0.026(6)	0.037(7)	0.030(7)	-0.003(6)	0.005(5)	-0.002(5)	0.031(3)
O10	O	0.5415(9)	0.3021(15)	0.8318(9)	0.027(6)	0.067(9)	0.028(7)	-0.019(7)	0.000(5)	0.008(6)	0.041(3)
OH11	OH	0.5793(10)	0.1470(16)	0.9844(13)	0.051(8)	0.034(8)	0.120(13)	0.034(8)	0.000(8)	0.003(6)	0.071(5)
O12	O	0.3980(8)	0.2902(13)	0.9444(8)	0.024(5)	0.050(7)	0.025(6)	0.002(5)	0.001(4)	-0.003(5)	0.033(3)
O13	O	0.8705(8)	0.4053(12)	0.5821(8)	0.023(5)	0.026(7)	0.017(6)	-0.001(5)	0.006(4)	0.003(5)	0.022(3)
OH14	OH	0.9418(9)	0.3442(14)	0.4257(8)	0.039(6)	0.038(7)	0.014(6)	0.008(5)	0.003(5)	0.011(6)	0.031(3)
O15	O	0.0738(8)	0.4110(11)	0.5916(8)	0.023(6)	0.021(5)	0.032(6)	-0.006(5)	0.004(4)	-0.003(4)	0.025(2)
O16	O	0.9726(8)	0.1649(12)	0.5720(8)	0.033(6)	0.020(6)	0.026(6)	0.003(5)	0.010(5)	0.002(5)	0.026(3)
O17	O	0.8663(8)	0.1185(12)	0.0146(8)	0.031(6)	0.024(7)	0.016(6)	-0.003(5)	0.008(5)	0.004(5)	0.023(3)
O18	O	0.7914(8)	0.3399(12)	-0.0295(8)	0.035(6)	0.021(6)	0.014(6)	0.005(5)	0.006(4)	0.010(5)	0.023(2)
O19	O	0.8251(8)	0.1509(12)	0.2024(7)	0.030(6)	0.023(6)	0.010(5)	0.004(5)	0.000(4)	0.001(5)	0.022(2)
O20	O	0.7518(8)	0.3725(12)	0.1594(8)	0.030(6)	0.019(6)	0.017(6)	0.000(5)	0.003(5)	0.001(5)	0.022(2)
O21	O	0.9256(8)	0.1088(14)	0.7669(9)	0.026(6)	0.042(8)	0.030(7)	-0.005(6)	0.009(5)	-0.002(5)	0.033(3)
O22	O	0.7020(9)	0.3907(12)	0.4131(7)	0.045(7)	0.032(7)	0.010(6)	-0.010(5)	-0.005(5)	0.001(5)	0.031(3)
OW1	H <sub>2</sub> O	0.2932(8)	0.4224(11)	0.0995(8)	0.053(6)	0.030(6)	0.039(6)	0.006(5)	0.015(5)	0.009(5)	0.040(2)
OW2	H <sub>2</sub> O	0.4008(7)	0.2873(11)	0.6592(7)	0.033(5)	0.050(6)	0.023(5)	-0.005(5)	-0.002(4)	0.007(5)	0.036(2)
OW3	H <sub>2</sub> O	0.2608(8)	0.4365(11)	0.7834(7)	0.038(5)	0.047(6)	0.025(5)	-0.004(5)	-0.001(4)	0.002(5)	0.038(2)
OW4	H <sub>2</sub> O	0.2442(8)	0.3156(12)	0.4763(7)	0.041(6)	0.059(7)	0.022(5)	-0.013(5)	-0.003(4)	-0.001(5)	0.042(3)
OW5	H <sub>2</sub> O	0.2032(8)	0.1535(12)	0.6752(9)	0.040(6)	0.035(6)	0.072(8)	0.012(6)	-0.007(6)	-0.005(5)	0.051(3)
OW6	H <sub>2</sub> O	0.5365(10)	0.1273(16)	0.2458(11)	0.050(8)	0.054(9)	0.072(10)	-0.009(7)	0.015(7)	0.012(7)	0.058(4)
OW7	H <sub>2</sub> O	0.0843(9)	0.3680(16)	0.9005(10)	0.047(7)	0.054(8)	0.052(8)	-0.007(6)	0.004(6)	-0.012(6)	0.052(3)
OW8	H <sub>2</sub> O	0.4429(8)	0.3301(12)	0.4191(8)	0.034(5)	0.062(7)	0.044(6)	-0.007(6)	0.006(5)	-0.009(5)	0.047(3)
OW9	H <sub>2</sub> O	0.3088(11)	0.0462(15)	0.9971(11)	0.087(10)	0.059(8)	0.084(10)	0.009(8)	0.017(8)	-0.027(7)	0.076(4)
OW10	H <sub>2</sub> O	0.3403(9)	0.0377(12)	0.2984(9)	0.047(6)	0.040(6)	0.065(8)	0.000(6)	-0.001(6)	0.003(5)	0.052(3)

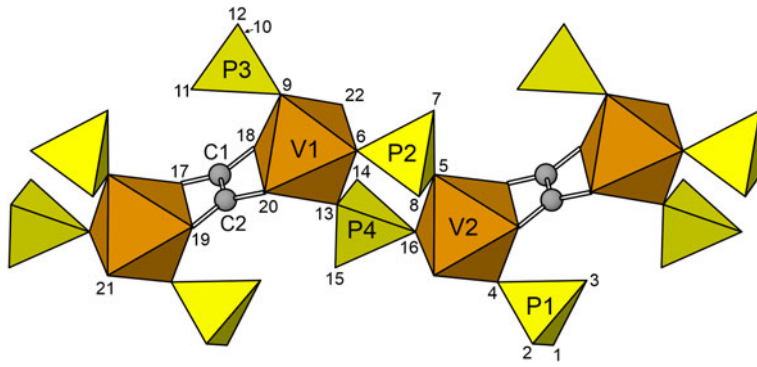
**Table 5.** Selected bond lengths (Å) and angles (°) for *relianseiteite*-(K).

Bond lengths				Proposed hydrogen bonding, distances and angles					
V1–O6	1.986(8)	V2–O4	2.017(7)	K1–O5	2.817(8)	OH3...O15	2.685(10)	OW1...O1	2.619(10)
V1–O9	1.996(7)	V2–O5	1.990(7)	K1–OH8	2.831(9)	OH8...O10	2.547(11)	OW1...O12	2.889(10)
V1–O13	2.000(7)	V2–O16	1.957(8)	K1–OH11	3.458(11)	OH11...O7	2.679(12)	O1–OW1–O12	121.0(3)
V1–O18	2.053(7)	V2–O17	2.286(7)	K1–OH14	3.293(9)	OH14...O2	2.525(11)		
V1–O20	2.266(7)	V2–O19	2.048(8)	K1–O16	3.460(7)				
V1–O22	1.599(7)	V2–O21	1.601(8)	K1–O17	2.789(8)	OW2...O7	2.835(10)	OW3...O1	2.920(10)
<V1–O>	1.983	<V2–O>	1.983	K1–O19	2.754(8)	OW2...O10	2.609(10)	OW3...O12	2.798(10)
				K1–O21	3.377(8)	O7–OW2–O10	88.2(3)	O1–OW3–O12	137.2(3)
P1–O1	1.495(7)	P2–O5	1.515(7)	K1–O22	2.841(8)				
P1–O2	1.531(7)	P2–O6	1.523(8)	K1–OW6	2.918(9)	OW4...O2	2.673(9)	OW5...O4	2.906(10)
P1–OH3	1.599(7)	P2–O7	1.495(8)	<K1–O>	3.054	OW4...OW8	2.715(10)	OW5...OW10	2.737(10)
P1–O4	1.537(7)	P2–OH8	1.573(8)			O2–OW4–OW8	118.6(3)	O4–OW5–OW10	83.6(3)
<P1–O>	1.541	<P2–O>	1.527	K2–OH3	3.155(8)				
				K2–O6	3.232(7)	OW6...O7	3.092(14)	OW7...O15	3.245(12)
P3–O9	1.544(7)	P4–O13	1.509(7)	K2–OH8	3.299(11)	OW6...OW10	2.775(11)	OW7...OW3	2.976(11)
P3–O10	1.504(7)	P4–OH14	1.579(8)	K2–O13	2.831(8)	O7–OW6–OW10	99.2(4)	O15–OW7–OW3	114.9(3)
P3–OH11	1.562(7)	P4–O15	1.541(8)	K2–OH14	2.819(8)				
P3–O12	1.522(7)	P4–O16	1.532(8)	K2–O18	2.748(8)	OW8...O7	3.058(13)	OW9...O7	3.340(12)
<P3–O>	1.533	<P4–O>	1.540	K2–O20	2.786(8)	OW8...O9	2.879(11)	OW9...O12	2.615(12)
				K2–O21	2.930(9)	O7–OW8–O9	94.7(3)	O7–OW9–O12	92.0(3)
				K2–O22	3.267(9)				
Mg–O15	2.052(7)	K3–O6	2.929(9)	K2–OW7	2.869(9)	OW10...O1	2.672(10)		
Mg–OW1	2.131(7)	K3–O9	2.895(9)	<K2–O>	2.994	OW10...OW9	2.837(13)		
Mg–OW2	2.091(7)	K3–O10	2.866(10)			O1–OW10–OW9	110.6(4)		
Mg–OW3	2.167(7)	K3–O20	2.877(8)						
Mg–OW4	2.039(7)	K3–O22	2.987(8)	K4–O2	2.759(8)				
Mg–OW5	2.043(8)	K3–OW1	3.192(8)	K4–O4	2.893(8)				
<Mg–O>	2.087	K3–OW2	3.112(8)	K4–O16	2.976(8)				
		K3–OW6	2.758(11)	K4–O17	2.855(8)				
C1–C2	1.531(9)	K3–OW8	3.295(8)	K4–O21	2.861(9)				
C1–O17	1.239(13)	<K3–O>	2.990	K4–OW7	2.849(11)				
C1–O18	1.260(12)			K4–OW9	2.871(10)				
C2–O19	1.234(13)			<K4–O>	2.866				
C2–O20	1.257(12)								

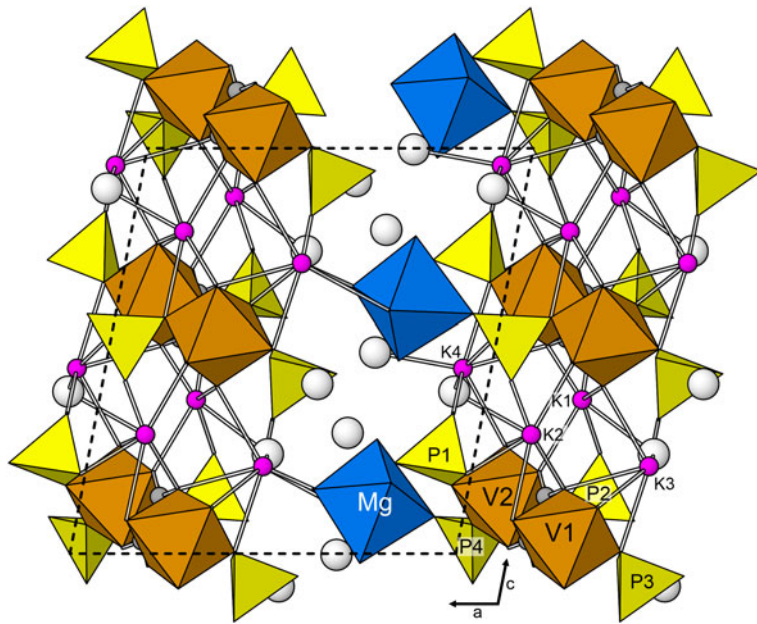
**Table 6.** Bond-valence analysis for *relianseiteite*-(K). Values are in valence units (vu).

	V1	V2	Mg	P1	P2	P3	P4	C1	C2	K1	K2	K3	K4	Hydrogen bonds		Σ
														Donated	Accepted	
O1				1.38											0.27, 0.15, 0.24	2.04
O2				1.26											0.35, 0.24	2.05
OH3				1.06							0.06			–0.23		0.89
O4		0.52		1.24									0.14		0.15	2.05
O5		0.56			1.31					0.16						2.03
O6	0.56				1.29						0.05	0.12				2.03
O7					1.38										0.24, 0.17, 0.11, 0.12, 0.09	2.11
OH8					1.14					0.15	0.04			–0.33		1.01
O9	0.55					1.22						0.13			0.16	2.06
O10						1.35						0.15			0.33, 0.28	2.10
OH11						1.17				0.03				–0.24		0.96
O12						1.29									0.16, 0.18, 0.28	1.91
O13	0.54						1.33				0.14					2.01
OH14							1.12			0.05	0.15			–0.35		0.97
O15			0.37				1.23								0.23, 0.10	1.93
O16		0.61					1.26			0.03			0.11			2.01
O17		0.25						1.49		0.17			0.16			2.07
O18	0.47							1.41			0.18					2.06
O19		0.47							1.51	0.19						2.17
O20	0.26								1.42		0.16	0.14				1.98
O21		1.62								0.04	0.11		0.15			1.92
O22	1.63									0.15	0.05	0.11				1.93
OW1			0.31									0.06		–0.27, –0.16		–0.06
OW2			0.34									0.08		–0.17, –0.28		–0.03
OW3			0.28											–0.18, –0.15	0.14	0.08
OW4			0.38											–0.24, –0.22		–0.08
OW5			0.37											–0.15, –0.21		0.01
OW6										0.12		0.19		–0.11, –0.19		0.01
OW7											0.13		0.16	–0.10, –0.14		0.06
OW8												0.05		–0.12, –0.16	0.22	–0.01
OW9													0.15	–0.09, –0.28		–0.04
OW10														–0.24, –0.17	0.21, 0.19	–0.01
Σ	4.01	4.03	2.05	4.94	5.12	5.03	4.94	2.90	2.93	1.08	1.08	1.03	1.08			

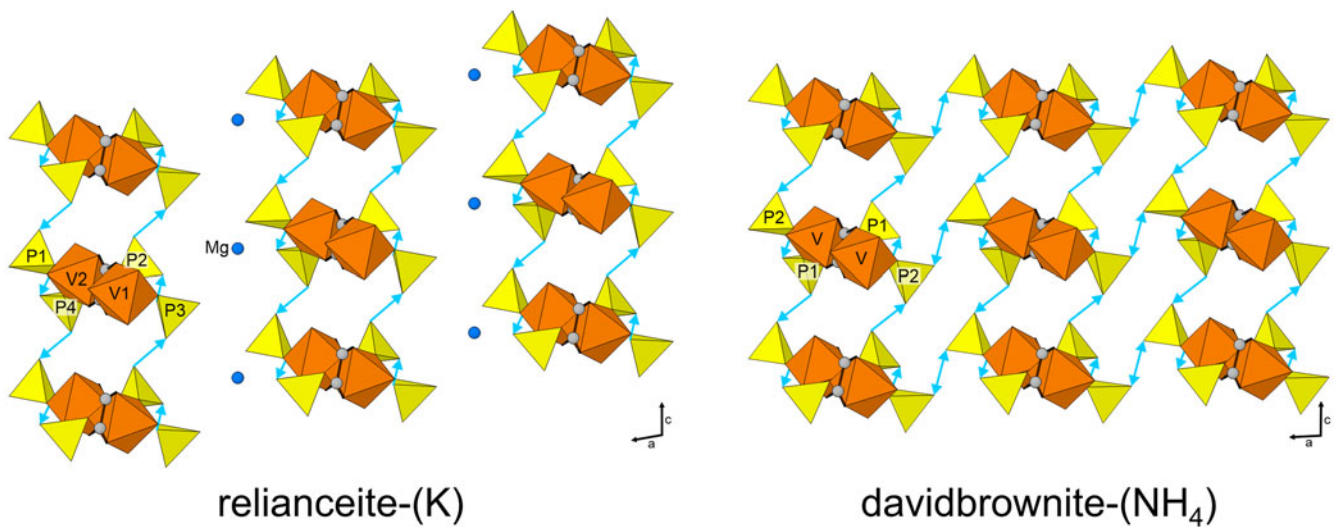
Bond-valence parameters for  $\text{NH}_4^+\text{-O}$  are from Garcia-Rodriguez *et al.* (2000); all others are from Gagné and Hawthorne (2015). The K/N sites were modelled using refined occupancies. Hydrogen-bond strengths are based on O–O distances according to the relation of Ferraris and Ivaldi (1988).



**Fig. 4.** The decorated chain in the relianceite-(K) structure. The O sites are numbered. The view is along  $[10\bar{1}]$  with  $[010]$  horizontal.



**Fig. 5.** The relianceite-(K) structure viewed down  $[010]$ . The unit cell outline is shown with dashed lines.



**Fig. 6.** Hydrogen-bond linkages between the chains in the structures of relianceite-(K) and davidbrownite-(NH<sub>4</sub>) viewed down  $[010]$ . The hydrogen bonds are shown as turquoise-coloured lines pointing from the donating OH group toward the receiving O atom. The double-ended arrow indicates the symmetrical H-bond between OH8 anions.

ascribed as O, OH or H<sub>2</sub>O. Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and a bond-valence analysis in Table 6. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

## Discussion of the structure

The structure of relianceite-(K) includes four large cation sites coordinated by O (O, OH and/or H<sub>2</sub>O) sites: K1 (ten coordinated), K2 (ten coordinated), K3 (nine coordinated) and K4 (seven coordinated). One octahedrally coordinated Mg site is surrounded by one O site and five H<sub>2</sub>O sites. There are four P sites, P1, P2, P3 and P4, all tetrahedrally coordinated by three O and one OH. One oxalate (C<sub>2</sub>O<sub>4</sub>) group includes two independent C sites, C1 and C2, and four independent O sites. The two V<sup>4+</sup> sites, V1 and V2, are both octahedrally coordinated by O sites. Each of the V<sup>4+</sup> bonds to three O atoms shared by phosphate groups with V–O bond distances ranging from 1.957 to 2.017 Å, two O atoms shared with the oxalate C<sub>2</sub>O<sub>4</sub> group with longer V–O bonds from 2.048 to 2.286 Å, and one O atom that forms a short vanadyl V=O bond of 1.599 and 1.601 Å. The longest V–O bonds in each octahedron is *trans* to the short vanadyl bond, giving typical [1+4+1]-coordinations (Schindler *et al.*, 2000).

The structural unit is a chain along **b** constructed of VO<sub>6</sub>-octahedra, PO<sub>3</sub>OH tetrahedra and C<sub>2</sub>O<sub>4</sub> oxalate groups. In this chain, pairs of VO<sub>6</sub> octahedra, V1O<sub>6</sub> and V2O<sub>6</sub>, are linked by the bridging oxalate group, forming [V<sub>2</sub>C<sub>2</sub>O<sub>12</sub>] dimers. Two PO<sub>3</sub>OH tetrahedra, P2O<sub>3</sub>OH and P4O<sub>3</sub>OH, form a double bridge between the VO<sub>6</sub> octahedra, thereby linking the [V<sub>2</sub>C<sub>2</sub>O<sub>12</sub>] dimers into the chain. Additional PO<sub>3</sub>OH tetrahedra, P1O<sub>3</sub>OH and P3O<sub>3</sub>OH, decorate the chain. The decorated (V<sup>4+</sup>O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)(PO<sub>3</sub>OH)<sub>4</sub> chain (Fig. 4) is identical to that in the structure of davidbrownite-(NH<sub>4</sub>), (NH<sub>4</sub>K)<sub>5</sub>(V<sup>4+</sup>O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)[PO<sub>2.75</sub>(OH)<sub>1.25</sub>]<sub>4</sub>·3H<sub>2</sub>O (Kampf *et al.*, 2019a). The O site (O15) of the MgO(H<sub>2</sub>O)<sub>5</sub> octahedron is the O site of the P4O<sub>3</sub>OH tetrahedron that does not link to V1 or V2. It can be considered a distant decoration on the (V<sup>4+</sup>O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)(PO<sub>3</sub>OH)<sub>4</sub> chain. As seen in Fig. 5, the chains are linked to each other through an extensive system of K/NH<sub>4</sub>–O bonds and hydrogen bonds.

Both relianceite-(K) and davidbrownite-(NH<sub>4</sub>) contain acid-phosphate groups that deliver strong intra- and inter-chain H-bonds (i.e. OH...O<sub>A</sub> distances 2.47–2.68 Å). Both structures contain two similar intra-chain H-bonds linking vertices of bridging and decorating P tetrahedra within the chain, and two inter-chain H-bonds that link decorating P tetrahedra of adjacent chains along [001] (Fig. 6). Davidbrownite-(NH<sub>4</sub>) contains additional OH bonded to its decorating P tetrahedra in the form of a single H atom bridging symmetrically equivalent OH<sup>8</sup> anions on adjacent chains along [100]. In relianceite-(K), the neighbouring chains are more distant from each other in the [100] direction, and a Mg atom is located between chains in this region of the structure. The relative positioning of chains in the {010} plane differs between the two structures in relation to their different inter-chain connectivity, with relianceite-(K) having a greater β angle and **a**-translation.

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