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Disordered $LiZnVO_4$ with a phenacite structure

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Key indicators: single-crystal X-ray study; T = 298 K; mean σ(V–O) = 0.001 Å; disorder in main residue; R factor = 0.024; wR factor = 0.055; data-to-parameter ratio = 23.5.

Single crystals of lithium zinc vanadate, $LiZnVO_4$, were grown by the flux method. The structural type of this vanadate is characterized by a three-dimensional arrangement of tetrahedra sharing apices in an $LiZnVO_4$ network. This arrangement contains three different tetrahedra, namely one [VO_4] and two disordered mixed-site [Li/ZnO_4] tetrahedra. The resulting lattice gives rise to hexagonal channels running along the [0001] direction. Both sites in the mixed-site [Li/ZnO_4] tetrahedra are occupied by a statistical mixture of lithium and zinc with a 1:1 ratio. Therefore, $LiZnVO_4$ appears to be the first vanadate known to crystallize with a disordered phenacite structure. Moreover, the resulting values of calculated bond valences (Li = 1.083, Zn = 2.062 and V = 5.185) tend to confirm the structural model.

Related literature

For related structural studies, see: Hartmann (1989); Capsoni *et al.* (2006); Zachariasen (1971). For compounds with the same structural type, see: Bu *et al.* (1996); Elammari & Elouadi (1989); Elouadi & Elammari (1990); Jensen *et al.* (1998). For bond-valence calculations, see: Brown & Altermatt (1985).

Experimental

Crystal data

$LiZnVO_4$
M_r = 187.25
Trigonal, $R\bar{3}$
a = 14.107 (3) Å
c = 9.441 (2) Å
V = 1627.1 (6) $Å^3$
Z = 18
Mo $K\alpha$ radiation
μ = 9.06 mm^{-1}
T = 298 K
0.14 × 0.12 × 0.10 mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.292, T_{max} = 0.404
9709 measured reflections
1622 independent reflections
1213 reflections with $I > 2\sigma(I)$
R_{int} = 0.070

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.055
S = 1.04
1622 reflections
69 parameters
$\Delta\rho_{max}$ = 0.51 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.53 e $Å^{-3}$

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2291).

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S1. Comment

Our particular interest here is to investigate the form nature of the crystallized phase and determine the structural type that could result from the association of small size cations likely to enter under normal conditions of pressure and temperature, tetrahedral cavities of oxides like in phenacite Be_2SiO_4 network (Hartmann, 1989; Zachariasen, 1971). The compounds currently known to crystallize with such structural type are $LiZnPO_4$ (Bu *et al.*, 1996; Elammari & Elouadi, 1989; Elouadi & Elammari, 1990) and $LiZnAsO_4$ (Jensen *et al.*, 1998).

The structural type of the title compound, related to the phenacite structure, could be described (Fig.1) as three dimensional arrangement of $[MO_4]$ tetrahedra (M= Li/Zn or V) sharing apices. The arrangement concerns three different types of tetrahedra $[VO_4]$ and two disordered sites $[Li/ZnO_4]$ which give rise to an overall disordered phenacite structure. When viewed along the c axis, the packing of $[MO_4]$ tetraherdra results in two types of tunnels: large hexagonal tunnels surrounded by six lozenge like channels (rings of four tetrahedra). Similar description has recently been reported by Capsoni *et al.* (2006) using a powder x-ray diffraction data of $LiZnVO_4$. However, a careful observation of the two models can highlights the difference between our two results. Indeed, in addition to the difference of the lengths of chemical bonds, the occupancy rate of cationic Wycoff sites is different. Thus, in our model, there is only a disorder between Li and Zn with a statistical distribution of both ions on the two crystallographic sites, while the third site is only occupied by vanadium cation. Furthermore, A bond-valence analysis (Li <1.083>, Zn<2.062> and <V<5.185>) based on the empirical formula proposed by Brown & Altermatt (1985) is in favor of this model . The cationic disorder mentioned by Capsoni *et al.* could be seen as due to preparation methods. The powder used was slowly cooled from 853 K after 24 h sintering. Whereas, the growth of our crystal, from a flux melted at 1073 k and slowly cooled with a rate of 5 K h-1. Thus the resulting sintering of our crystal was much longer. A more ordred system is then to be expected.

When such structural type is seen as a close packing of oxygen anions, it appears as a lacunar hexagonal close packing of O^{2-} ions. Fig.2 shows a typical oxygen layer and the elevation of such oxygen plans as successively stacked (ABAB···) along [0001]. The coordination sphere of all cations is of tetrahedral type. The analysis of oxygen environment shows a regular triangular cavity for O^{2-} anions with an average edge length of <V—Li/Zn> = 3.240 Å.

In the case of the present form of $LiZnVO_4$, the disordered phenacite structure was attributed to the existence of a mixed tetrahedral site [Li/ZnO4] occupied by both Li and Zn. The resulting space group is R-3. $LiZnVO_4$ is probably the first vanadate known to crystallize with a disordered phenacite structure.

S2. Experimental

Prior to the crystal growth, pulverulent samples of the compound $LiZnVO_4$ and the flux $LiVO_3$ are synthesized by the regular solid state reaction according to the following reactions:

$Li_2CO_3 + 2ZnO + V_2O_5 \longrightarrow 2LiZnVO_4 + CO_2$ $Li_2CO_3 + V_2O_5 \longrightarrow 2LiVO_3 + CO_2$

Single crystal of the monovanadate $LiZnVO_4$ were grown from a bath of equimolar mixture of freohly prepared powders of $LiZnVO_4$ and $LiVO_3$. The starting mixture was thoroughly ground before to be melted at 1073 K in a platinum crucible and slowly cooled with a rate of 5 K h-1 to 773 K. The furnace was then switched off and the whole system naturally cooled down to room temperature. Single crystal s were collected from the crucible after dissolwing the flux in warmed water.

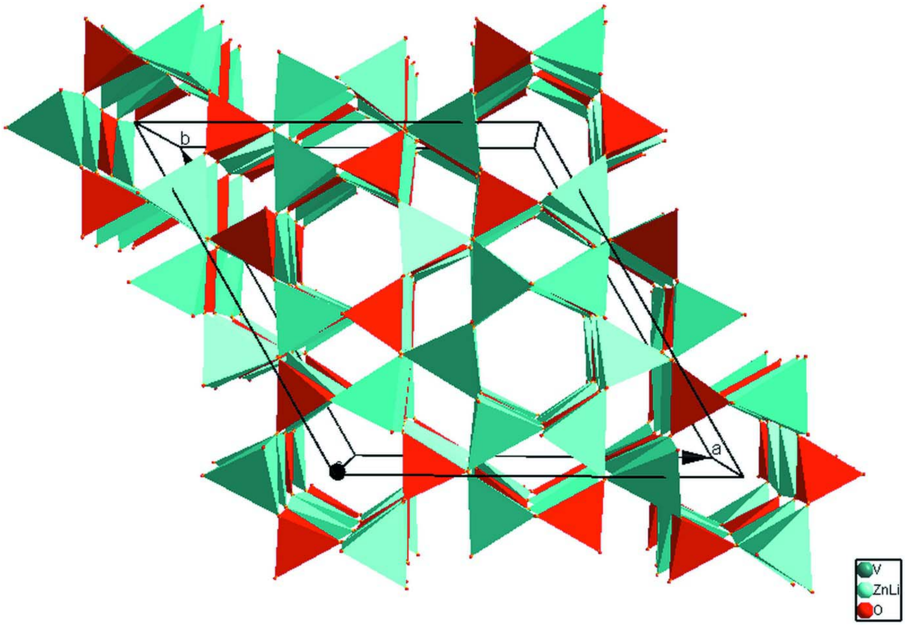

Figure 1

A three-dimensional view of $LiZnVO_4$ crystal structure, showing tunnels runnig along the c axis.

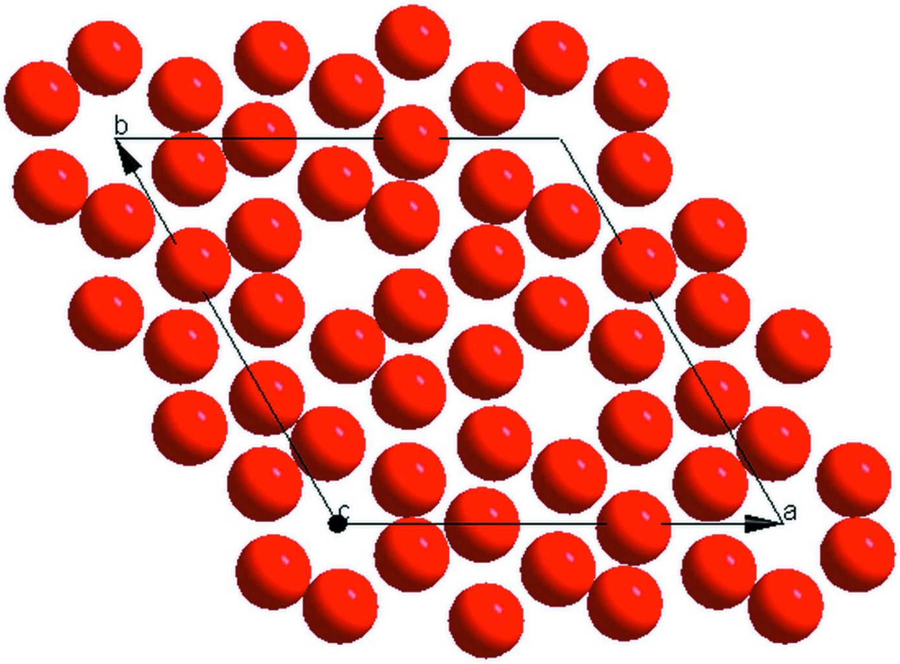

Figure 2

Partial projection of the crystal structure on (0 0 1), showing lacunar hexagonal close packing of O^{2-} ions.

lithium zinc vanadate

Crystal data

$LiZnVO_4$
M_r = 187.25
Trigonal, $R\overline{3}$
Hall symbol: -R 3
a = 14.107 (3) Å
c = 9.441 (2) Å
V = 1627.1 (6) Å^3
Z = 18
F(000) = 1584
D_x = 3.440 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9709 reflections
θ = 10–30°
μ = 9.06 mm^{-1}
T = 298 K
Prism, pale yellow
0.14 × 0.12 × 0.10 mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.292, T_{max} = 0.404
9709 measured reflections
1622 independent reflections
1213 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 35.2°, θ_{min} = 4.0°
$h = -22 \rightarrow 22$
$k = -22 \rightarrow 22$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.055
S = 1.04
1622 reflections
69 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0124P)^2 + 2.5069P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0088 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement on F^2 for ALL reflections except for 0 with very negative F^2 or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
V1	0.454581 (17)	0.138171 (16)	0.08352 (2)	0.00790 (7)	

Zn1	0.45273 (2)	0.14015 (2)	−0.24915 (3)	0.01132 (7)	0.50
Li1	0.45273 (2)	0.14015 (2)	−0.24915 (3)	0.01132 (7)	0.50
Zn2	0.64622 (2)	0.12175 (3)	0.24882 (3)	0.01150 (7)	0.50
Li2	0.64622 (2)	0.12175 (3)	0.24882 (3)	0.01150 (7)	0.50
O1	0.34102 (7)	0.01142 (7)	0.08427 (11)	0.01335 (17)	
O2	0.56475 (8)	0.11882 (9)	0.08215 (10)	0.01353 (17)	
O3	0.45578 (8)	0.20780 (8)	−0.06565 (10)	0.01419 (18)	
O4	0.45936 (8)	0.20728 (8)	0.23409 (10)	0.01377 (17)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.00918 (10)	0.00812 (10)	0.00692 (9)	0.00472 (8)	−0.00012 (6)	−0.00004 (6)
Zn1	0.01190 (12)	0.01217 (13)	0.01038 (12)	0.00637 (10)	0.00052 (9)	0.00069 (9)
Li1	0.01190 (12)	0.01217 (13)	0.01038 (12)	0.00637 (10)	0.00052 (9)	0.00069 (9)
Zn2	0.01159 (13)	0.01368 (13)	0.01016 (12)	0.00701 (10)	0.00005 (9)	0.00037 (9)
Li2	0.01159 (13)	0.01368 (13)	0.01016 (12)	0.00701 (10)	0.00005 (9)	0.00037 (9)
O1	0.0109 (4)	0.0102 (4)	0.0180 (4)	0.0046 (3)	−0.0010 (3)	0.0000 (3)
O2	0.0121 (4)	0.0198 (4)	0.0115 (3)	0.0101 (3)	−0.0005 (3)	−0.0005 (3)
O3	0.0219 (5)	0.0120 (4)	0.0103 (3)	0.0096 (3)	−0.0007 (3)	0.0009 (3)
O4	0.0209 (4)	0.0125 (4)	0.0104 (4)	0.0102 (4)	0.0003 (3)	−0.0004 (3)

Geometric parameters (Å, º)

V1—O1	1.7027 (10)	Zn2—O2	1.9368 (10)
V1—O4	1.7059 (10)	Zn2—O4$^{\rm x}$	1.9495 (10)
V1—O2	1.7071 (10)	Zn2—O4$^{\rm xi}$	1.9676 (11)
V1—O3	1.7123 (10)	Zn2—Li1$^{\rm iv}$	3.1441 (8)
V1—Li2$^{\rm i}$	3.1568 (7)	Zn2—Zn1$^{\rm iv}$	3.1441 (8)
V1—Li1$^{\rm ii}$	3.1719 (8)	Zn2—Li1$^{\rm viii}$	3.2314 (8)
V1—Li2$^{\rm iii}$	3.2409 (8)	Zn2—Li2$^{\rm i}$	3.2675 (7)
V1—Li1$^{\rm iv}$	3.2523 (6)	Zn2—Li2$^{\rm x}$	3.2676 (7)
V1—Li2$^{\rm v}$	3.2978 (7)	O1—Li2$^{\rm iii}$	1.9294 (11)
V1—Li1$^{\rm vi}$	3.3232 (7)	O1—Zn2$^{\rm iii}$	1.9294 (11)
Zn1—O2$^{\rm vi}$	1.9410 (10)	O1—Zn1$^{\rm ii}$	1.9442 (11)
Zn1—O1$^{\rm vii}$	1.9441 (11)	O1—Li1$^{\rm ii}$	1.9442 (11)
Zn1—O3$^{\rm iv}$	1.9588 (11)	O2—Li1$^{\rm iv}$	1.9411 (10)
Zn1—O3	1.9679 (11)	O2—Zn1$^{\rm iv}$	1.9411 (10)
Zn1—Zn2$^{\rm vi}$	3.1441 (8)	O3—Li1$^{\rm vi}$	1.9587 (11)
Zn1—Li2$^{\rm vi}$	3.1441 (8)	O3—Zn1$^{\rm vi}$	1.9587 (11)
Zn1—Li2$^{\rm viii}$	3.2314 (8)	O4—Li2$^{\rm i}$	1.9496 (10)
Zn1—Li1$^{\rm vi}$	3.2765 (7)	O4—Zn2$^{\rm i}$	1.9496 (10)
Zn1—Li1$^{\rm iv}$	3.2766 (7)	O4—Li2$^{\rm v}$	1.9676 (11)
Zn2—O1$^{\rm ix}$	1.9294 (11)	O4—Zn2$^{\rm v}$	1.9676 (11)
O1—V1—O4	110.14 (5)	O2$^{\rm vi}$—Zn1—O3	115.71 (4)
O1—V1—O2	106.61 (5)	O1$^{\rm vii}$—Zn1—O3	106.57 (4)
O4—V1—O2	108.58 (5)	O3$^{\rm iv}$—Zn1—O3	110.08 (5)

O1—V1—O3	109.88 (5)	O1$^{\text{ix}}$—Zn2—O2	111.98 (5)
O4—V1—O3	111.80 (5)	O1$^{\text{ix}}$—Zn2—O4$^{\text{x}}$	108.76 (4)
O2—V1—O3	109.69 (5)	O2—Zn2—O4$^{\text{x}}$	117.26 (4)
O2$^{\text{vi}}$—Zn1—O1$^{\text{vii}}$	109.39 (5)	O1$^{\text{ix}}$—Zn2—O4$^{\text{xi}}$	102.55 (4)
O2$^{\text{vi}}$—Zn1—O3$^{\text{iv}}$	106.12 (4)	O2—Zn2—O4$^{\text{xi}}$	107.30 (4)
O1$^{\text{vii}}$—Zn1—O3$^{\text{iv}}$	108.84 (4)	O4$^{\text{x}}$—Zn2—O4$^{\text{xi}}$	107.87 (5)

Symmetry codes: (i) *y*+1/3, −*x*+*y*+2/3, −*z*+2/3; (ii) −*x*+*y*+2/3, −*x*+1/3, *z*+1/3; (iii) *x*−*y*−1/3, *x*−2/3, −*z*+1/3; (iv) *x*−*y*+1/3, *x*−1/3, −*z*−1/3; (v) −*x*+*y*+1, −*x*+1, *z*; (vi) *y*+1/3, −*x*+*y*+2/3, −*z*−1/3; (vii) −*y*+1/3, *x*−*y*−1/3, *z*−1/3; (viii) −*x*+1, −*y*, −*z*; (ix) *y*+2/3, −*x*+*y*+1/3, −*z*+1/3; (x) *x*−*y*+1/3, *x*−1/3, −*z*+2/3; (xi) −*y*+1, *x*−*y*, *z*.