Coordination of Vanadium(5+) in Solid Solutions MgV₂O₆–CaV₂O₆ and ZnV₂O₆–CaV₂O₆

Staffan Hansen[a],* and Jerker Nilsson[b]

[a]National Center for HREM, Inorganic Chemistry 2, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden and [b]Chemical Technology, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

Hansen, S. and Nilsson, J., 1996. Coordination of Vanadium(5+) in Solid Solutions MgV₂O₆–CaV₂O₆ and ZnV₂O₆–CaV₂O₆. Acta Chem. Scand. 50: 512–515 © Acta Chemica Scandinavica 1996.

The unit-cell parameters of phases in the systems MgV₂O₆–CaV₂O₆ and ZnV₂O₆–CaV₂O₆ have been determined at room temperature by powder X-ray diffraction. Two brannerite-related phases (both monoclinic, $C2/m$) were observed, i.e. α (a low-temperature form with $5+1$ coordination of V and a monoclinic angle of ca. 112°) and β (a high-temperature form with five-coordinated V and monoclinic angle $\approx 105°$). $Mg_{1-x}Ca_xV_2O_6$: $0 < x < 0.35$–0.40 α; 0.35–$0.40 < x < 1$ β; and $Zn_{1-x}Ca_xV_2O_6$: $0 < x < 0.40$ α; $0.40 < x < 0.50$ $\alpha + \beta$; $0.50 < x < 1$ β. Predicted bond valences and bond lengths were calculated from the connectivity matrices of MV_2O_6 (M = Mg, Zn, Ca). A comparison with observed bond lengths (single-crystal literature data) indicates that vanadium is effectively five-coordinated in both α and β. If isostructural compounds are required to possess the same net of primary bonds, then these vanadates are not isostructural with brannerite. Instead, α and β represent a distinct structure type.

The brannerite type of structure was discovered in 1966 by Ruh and Wadsley,[1] and the crystal structure of synthetic UTi_2O_6 has been refined.[2] In this structure uranium(4+) occupies a rather regular oxygen octahedron with distances (d) U–O of 2.25 Å $(2\times)$ and 2.30 Å $(4\times)$, while titanium(4+) occupies another, less regular, octahedron of oxygens with $d(\text{Ti–O}) = 1.85$–2.10 Å. Several vanadates of divalent metals have crystal structures that are similar to the brannerite type. In these the divalent metal ion M^{2+} occupies the same type of site as U^{4+} in brannerite, while V^{5+} occupies a position corresponding to the Ti^{4+} site. The oxygen coordination of the V atom is, however, severely distorted, and is usually described as a $5+1$ or five-coordination.

Many of these MV_2O_6 compounds exhibit a reversible phase transition as a function of temperature.[3,4] In the low-temperature form, hereafter designated α, vanadium exhibits the aforementioned distorted octahedral $5+1$ coordination. In the high-temperature form β, vanadium is in a well defined trigonal bipyramid of five oxygen atoms. Both forms (α and β) are monoclinic ($C2/m$), and the transition $\alpha \rightarrow \beta$ is accompanied by an increase in the lattice parameters a, b and c, while the monoclinic angle typically decreases from 111–112° in the α-form to 104–105° in the β-form. The overall result is an increase in the cell volume, as expected. Single-crystal data, taken from the literature, for MgV_2O_6,[5] ZnV_2O_6[6] and CaV_2O_6[3]

are presented in Table 1. These three substances have been chosen since they exhibit very different temperature-dependent behaviour.[4] At room temperature α-MgV_2O_6 is stable, and it transforms to the β-form at 535 °C, which then melts at 765 °C. On the other hand, α-ZnV_2O_6 is stable all the way from room temperature to the melting point at 645 °C, while β-CaV_2O_6 is stable from room temperature to the melting point at 761 °C. Upon cooling of MgV_2O_6, the $\beta \rightarrow \alpha$ transition exhibits some hysteresis, i.e. the transition takes place at a temperature which is around 130 °C below the temperature recorded when heating.[4] Drawings of the brannerite type of structure and the vanadates α and β are to be found in several papers.[1–6]

The structures of MV_2O_6 (M = Mg, Zn, Ca) raise some interesting crystal chemical issues, e.g. long-standing problems of how to define central concepts such as

* To whom correspondence should be addressed.

Table 1. Room-temperature single-crystal data and residuals for MV_2O_6 (M = Mg, Zn, Ca) phases, monoclinic space group $C2/m$, $Z = 2$.

Compound Ref.	α-MgV₂O₆ 5	α-ZnV₂O₆ 6	β-CaV₂O₆ 3
a/Å	9.28	9.27	10.06
b/Å	3.50	3.52	3.67
c/Å	6.73	6.59	7.04
β/°	111.8	111.4	104.8
R	0.032	0.037	0.081

coordination number and structure type. Here we address some questions concerning the coordination of vanadium in MV$_2$O$_6$ (M = Mg, Zn, Ca). Firstly, the transition $\alpha \rightleftharpoons \beta$ as a function of composition is examined in the systems MgV$_2$O$_6$–CaV$_2$O$_6$ and ZnV$_2$O$_6$–CaV$_2$O$_6$. Secondly, we evaluate the coordination number of V^{5+} by calculation of the expected bond valences[7] using connectivity matrices with five- or six-coordinated vanadium. The expected bond lengths are then calculated[8] and compared to observed values.[3,5,6]

Experimental

Sample preparation. Samples in the two series MgV$_2$O$_6$–CaV$_2$O$_6$ and ZnV$_2$O$_6$–CaV$_2$O$_6$ were prepared from MgO (BDH, laboratory reagent), ZnCO$_3$ (Baker, analyzed), CaCO$_3$ (Merck, pA) and V$_2$O$_5$ (Riedel-de-Haën, pA). Preparations of (Mg,Ca)V$_2$O$_6$ were heated at 600 °C for 4 days with one intermittent grinding; they were then allowed to cool to 120 °C during a period of 5 h and were held overnight at this temperature. They were finally allowed to cool down to room temperature in 3 h. The (Zn,Ca)V$_2$O$_6$ samples were heated at 550 °C for 7 days with three intermittent grindings; they were subsequently cooled to 100 °C in 1 h and were held overnight at this temperature, followed by slow cooling to room temperature in 6 h.

Powder X-ray diffraction. The samples were mixed with silicon powder ($a = 5.430\,88$ Å) and were mounted on Scotch tape without previous grinding in order not to affect the crystallinity of the material, since these vanadates apparently cleave very easily and they are also known to undergo pressure-induced phase transitions.[3] X-Ray powder diffraction films were recorded at room temperature with a Guinier–Hägg camera using CuKα_1 radiation ($\lambda = 1.540\,56$ Å). Approximate unit-cell parameters were obtained from the reflections 020, 200, 003, 201 and 20−1, and they were then refined by the least-squares method.

Bond valence calculations. There are three crystallographically distinct oxygen atoms in MV$_2$O$_6$, designated O$_1$, O$_2$ and O$_3$. The following nearest neighbours (in brackets) are observed; Mg [O$_1$ (2 ×), O$_2$ (4 ×)]; V [O$_1$, O$_2$, O$_3$ (3 ×) and possibly O$_1$']; O$_1$ [M, V (possibly 2 ×)]; O$_2$ [M (2 ×), V]; O$_3$ [V (3 ×)]. We now assign a bond valence to each type of bond in the structure. As can be seen in the connectivity matrix in Table 2, there are five types of bond. For each atom, the sum of bond valences is put equal to the valence of that atom. This gives the five valence equations in Table 3, one for each atom, although only four of these equations are independent, since the atomic valence sum of the metals equals that of the oxygens. The necessary sixth equation is derived from the circuit indicated in the connectivity matrix (Table 2). The sixth equation in Table 3 corresponds to minimizing the difference between bond valences[7] around

Table 2. Connectivity matrix for MV$_2$O$_6$.[a]

	M	V
O$_1$	α	$-\ \gamma$
	|	|
O$_2$	β	$-\ \delta$
O$_3$		ε

[a] Greek letters designate bond valence values for specific metal–oxygen bonds.

Table 3. Valence equations for MV$_2$O$_6$.

|	Five-coordinated vanadium	Six-coordinated vanadium
O$_1$	$\alpha + \gamma = 2$	$\alpha + 2\gamma = 2$
O$_2$	$2\beta + \delta = 2$	$2\beta + \delta = 2$
O$_3$	$3\varepsilon = 2$	$3\varepsilon = 2$
M	$2\alpha + 4\beta = 2$	$2\alpha + 4\beta = 2$
V	$\gamma + \delta + 3\varepsilon = 5$	$2\gamma + \delta + 3\varepsilon = 5$
Circuit	$\alpha - \beta + \delta - \gamma = 0$	$\alpha - \beta + \delta - \gamma = 0$
Results		
	$\alpha = 3/7 \approx 0.43$	$\alpha = 1/6 \approx 0.17$
	$\beta = 2/7 \approx 0.29$	$\beta = 5/12 \approx 0.42$
	$\gamma = 11/7 \approx 1.57$	$\gamma = 11/12 \approx 0.92$
	$\delta = 10/7 \approx 1.43$	$\delta = 7/6 \approx 1.16$
	$\varepsilon = 2/3 \approx 0.67$	$\varepsilon = 2/3 \approx 0.67$

the four-membered circuit –O$_1$–M–O$_2$–V–. Inclusion of weights in the circuit equation[9] does not lead to a general improvement of the results and has not been used in the present case. The expected bond valences can now be calculated assuming a five- or six-coordinated V atom (Table 3). Expected bond lengths are then calculated using the expression $d = d_0 - 0.37$ Å ln v, where d is the bond length and v is the bond valence.[8] The empirical constant d_0 is set equal to 1.693 Å [Mg–O]; 1.704 Å [Zn–O]; 1.967 Å [Ca–O] and 1.803 Å [V^{5+}–O].

Results and discussion

Solid solutions. The unit-cell parameters of phases in the systems MgV$_2$O$_6$–CaV$_2$O$_6$ and ZnV$_2$O$_6$–CaV$_2$O$_6$ are given in Table 4. The variation of the cell volume as a function of mol% Ca is shown in Fig. 1 for (Mg,Ca)V$_2$O$_6$ and in Fig. 2 for (Zn,Ca)V$_2$O$_6$. In samples of (Mg,Ca)V$_2$O$_6$ prepared by cooling to room temperature, the α-form with 5+1 coordination of V is observed up to 35 mol% Ca, while at 40% the material has transformed to the β-form with coordination number 5. Both before and after this α→β transition, Vegard's law is apparently obeyed, cf. Table 4 and Fig. 1. These findings differ from an earlier investigation[10] of β-Mg$_{1-x}$Ca$_x$V$_2$O$_6$, which reported the compositional limits $0.30 < x < 1$ and a clearly non-linear relationship between unit-cell parameters and calcium content. The critical calcium content in (Mg,Ca)V$_2$O$_6$ and the linear compositional dependence of the lattice parameters observed here is, on the other hand, very similar to the

Table 4. Unit-cell parameters determined by powder X-ray diffraction.

x	a/Å	b/Å	c/Å	β/°
Mg$_{1-x}$Ca$_x$V$_2$O$_6$				
α 0.00	9.280(2)	3.488(1)	6.729(1)	111.77(2)
α 0.10	9.297(3)	3.503(1)	6.763(1)	111.91(2)
α 0.20	9.292(5)	3.519(2)	6.797(3)	111.94(4)
α 0.30	9.327(2)	3.534(1)	6.844(1)	112.23(2)
α 0.35	9.330(3)	3.540(1)	6.853(2)	112.25(3)
β 0.40	9.713(1)	3.601(1)	6.932(1)	104.94(2)
β 0.50	9.770(3)	3.613(1)	6.943(2)	104.95(3)
β 0.60	9.825(3)	3.625(1)	6.959(1)	104.99(2)
β 0.70	9.883(1)	3.638(1)	6.977(1)	104.94(1)
β 0.80	9.957(1)	3.650(1)	6.995(1)	104.91(1)
β 0.90	10.010(3)	3.662(1)	7.012(1)	104.87(2)
β 1.00	10.061(4)	3.672(1)	7.031(1)	104.83(2)
Zn$_{1-x}$Ca$_x$V$_2$O$_6$				
α 0.00	9.248(1)	3.530(1)	6.574(1)	111.38(1)
α 0.10	9.266(4)	3.525(2)	6.632(4)	111.54(4)
α 0.20	9.269(3)	3.545(2)	6.709(2)	111.51(4)
α 0.30	9.316(4)	3.553(1)	6.814(2)	112.18(4)
α 0.40	9.324(7)	3.555(2)	6.850(5)	112.27(6)
α 0.50	9.332(6)	3.562(5)	6.826(4)	112.10(4)
β 0.40	9.716(5)	3.608(1)	6.940(4)	104.93(6)
β 0.50	9.727(4)	3.612(1)	6.932(2)	105.02(3)
β 0.60	9.792(2)	3.622(1)	6.948(1)	105.03(1)
β 0.70	9.862(2)	3.634(1)	6.971(1)	105.01(1)
β 0.80	9.924(1)	3.644(1)	6.986(1)	104.94(1)
β 0.90	9.995(2)	3.661(1)	7.012(1)	104.87(1)
β 1.00	10.059(2)	3.673(1)	7.034(1)	104.84(1)
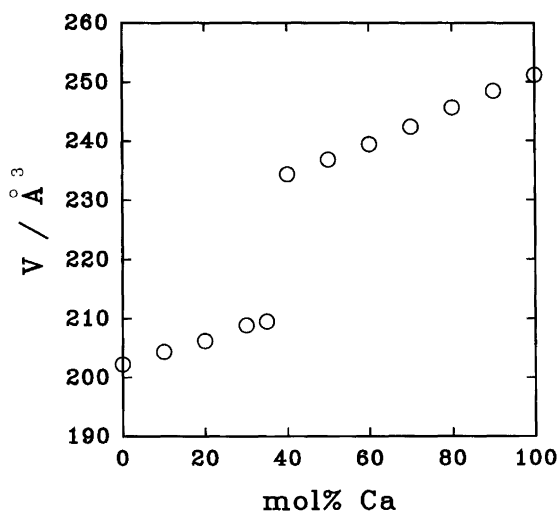
Fig. 1. Unit-cell volume as a function of composition in the system MgV$_2$O$_6$-CaV$_2$O$_6$.

results[11] in a study of β-Mn$_{1-x}$Ca$_x$V$_2$O$_6$, which was found for the compositions $0.37 < x < 1$ and that was obeying Vegard's law. In (Zn,Ca)V$_2$O$_6$, a two-phase gap is found in the interval 40–50 mol% Ca. This finding is to be expected, since pure ZnV$_2$O$_6$ remains in the α-form until melting, as opposed to pure MgV$_2$O$_6$, which undergoes a α→β transition before melting. A Vegard-law-type behaviour of the cell parameters in (Zn,Ca)V$_2$O$_6$ is again observed for both phases, cf. Table 4 and Fig. 2.
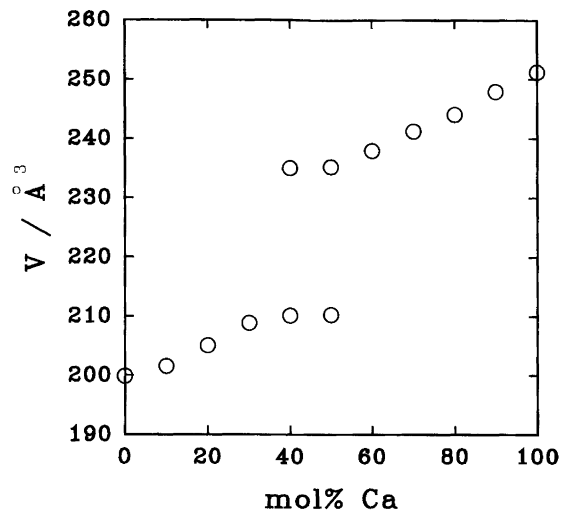
Fig. 2. Unit-cell volume as a function of composition in the system ZnV$_2$O$_6$-CaV$_2$O$_6$.

The linear relationship between unit-cell parameters and composition observed in the two series, for both α and β phases, indicates an almost ideal solid solution behaviour, without ordering tendencies for the divalent metal ions. The great similarity, both in positive slope and position, of the curve sections in Figs. 1 and 2 suggests that the distances Mg–O and Zn–O are nearly identical, while Ca–O distances are longer (cf. the d_0 values given above).

Vanadium coordination. Calculation of expected bond lengths is tried here as a novel approach to the problem of defining the coordination number (CN) of an atom in an irregular crystal environment. In Table 5 the expected bond lengths for MgV$_2$O$_6$ have been calculated for the two limiting cases, i.e. vanadium in five- or six-coordination. A comparison with the observed[5] bond lengths reveals that for five-coordination the fit is good, which is not the case for six-coordination. For CN(V) = 5 the observed distortion of the MgO$_6$ octahedron, with two short bonds and four long ones, is faithfully reproduced. For CN(V) = 6 the opposite distortion, with two long bonds and four short ones, is predicted. For five-

Table 5. Metal–oxygen distances (d) in α-MgV$_2$O$_6$, observed[5] or calculated using expected bond valences for five- or six-coordinated vanadium.

	Observed	Calculated	
		CN(V) = 5	CN(V) = 6
d(Mg–O$_1$) 2×	2.02	2.01	2.36
d(Mg–O$_2$) 4×	2.20	2.16	2.02
d(V–O$_1$)	1.67	1.64	1.84
d(V–O$_2$)	1.67	1.67	1.75
d(V–O$_3$) 2×	1.85	1.95	1.95
d(V–O$_3'$)	2.11	1.95	1.95
d(V–O$_1'$)	2.67	–	1.84
$\langle d$(V–O$_3$)$\rangle_3$	1.94	1.95	1.95

Table 6. Metal–oxygen distances (*d*) in α-ZnV$_2$O$_6$ and β-CaV$_2$O$_6$, observed[3,6] or calculated using expected bond valences for five-coordinated vanadium.

	α-ZnV$_2$O$_6$		β-CaV$_2$O$_6$	
	Observed	Calculated	Observed	Calculated
d(M–O$_1$) 2×	1.98	2.02	2.34	2.28
d(M–O$_2$) 4×	2.25	2.17	2.35	2.43
d(V–O$_1$)	1.68	1.64	1.61	1.64
d(V–O$_2$)	1.66	1.67	1.68	1.67
d(V–O$_3$) 2×	1.86	1.95	1.97	1.95
d(V–O$_3'$)	2.08	1.95	1.90	1.95
d(V–O$_1'$)	2.57	–	3.67	–
$\langle d(V-O_3)\rangle_3$	1.93	1.95	1.95	1.95

coordination the observed V–O distances, with two short bonds of 1.67 Å to O$_1$ and O$_2$, respectively, and the longer average distance of 1.94 Å of the three V–O$_3$ bonds, are reproduced. The observed splitting of the V–O$_3$ distances into 1.85 Å (2×) and 2.11 Å cannot be reproduced by the method[7] used here, since only one type of V–O$_3$ bond can be included. With six-coordinated vanadium the predicted V–O$_1$ and V–O$_2$ distances are slightly longer than the observed ones, while the predicted average V–O$_3$ distance does not change. This implies that the ladder formed by alternating V and O$_3$ atoms along *b* in the structure is insensitive to the nature of its crystal environment, as far as bond lengths are concerned. Finally the predicted distance to the sixth oxygen O$_1'$ is much too short. (Even the average V–O$_1$ distance observed is as long as 2.17 Å.)

By comparison of observed and predicted bond distances in α-MgV$_2$O$_6$ it can be concluded that vanadium is effectively five-coordinated, since no bonding effects which can be attributed to the influence of the sixth oxygen can be recognized in the experimental structure. If O$_1'$ did influence the bonding in the structure, one would, for example, expect the two Mg–O distances to become more equal.

In Table 6 the observed bond lengths and those calculated using five-coordinated vanadium in α-ZnV$_2$O$_6$ and β-CaV$_2$O$_6$ are compared. The fit is good for the zinc compound and somewhat less good for the calcium compound. The latter structure is not so well refined, cf. Table 1. In β-CaV$_2$O$_6$ there is nevertheless little doubt that vanadium is five-coordinated according to the list of observed distances in Table 6.

The bond valences in UTi$_2$O$_6$ can be determined by inspection. Both metal ions are tetravalent and six-coordinated, which gives a valence of 4/6 for all bonds. Since all oxygen atoms are three-coordinated, this value

without further adjustment provides satisfactory bond valence sums for the oxygens, i.e. $3 \times 4/6 = 2$. The uniform valence of the bonds suggests that the coordination polyhedra in UTi$_2$O$_6$ should be more regular than the ones in MV$_2$O$_6$ compounds, and this is also observed.[2] The predicted bond lengths are: $d(\text{U–O}) = 2.28$ Å (observed 2.25, 2.30 Å) and $d(\text{Ti–O}) = 1.97$ Å (observed 1.85–2.10 Å).

It has recently been argued[12] that for two compounds to be isostructural or for a crystal structure to be derivative of an aristotype structure, the same net of primary bonds must be present in both. In addition, isostructural compounds should also have the same stoichiometry and space group, and a derivative structure should exhibit the same stoichiometry as the aristotype and a symmetry with a subgroup relationship to the space group of the aristotype. In both the α- and β-forms of MV$_2$O$_6$, vanadium appears to be five-coordinated, M is six-coordinated, one oxygen is two-coordinated, while the other two are three-coordinated. In a proper brannerite both cations are six-coordinated, while all oxygens are in three-coordination. Thus, if the bond pattern is considered to be essential, we arrive at the conclusion that the vanadates discussed here are not brannerites. Instead they represent a unique structure type.

References

1. Ruh, R. and Wadsley, A. D. *Acta Crystallogr. 21* (1966) 974.
2. Szymański, J. T. and Scott, J. D. *Can. Miner. 20* (1982) 271.
3. Bouloux, J.-C., Perez, G. and Galy, J. *Bull. Soc. Fr. Miner. Cristallogr. 95* (1972) 130.
4. Mocała, K. and Ziółkowski, J. *J. Solid State Chem. 69* (1987) 299.
5. Ng, H. N. and Calvo, C. *Can. J. Chem. 50* (1972) 3619.
6. Andreetti, G. D., Calestani, G., Montenero, A. and Bettinelli, M. *Z. Kristallogr. 168* (1984) 53.
7. O'Keeffe, M. *Struct. Bonding (Berlin) 71* (1989) 162.
8. Brown, I. D. and Altermatt, D. *Acta Crystallogr., Sect. B41* (1985) 244.
9. O'Keeffe, M. *Acta Crystallogr., Sect. A46* (1990) 138.
10. Slobodin, B. V., Sharova, N. G. and Krasnenko, T. I. *Izv. Akad. Nauk SSSR, Neorg. Mater. 20* (1984) 688.
11. Krasnenko, T. I., Zabara, O. A., Surat, L. L. and Strepetov, S. V. *Izv. Akad. Nauk SSSR, Neorg. Mater. 23* (1987) 1407.
12. Baur, W. H. *Z. Kristallogr. 209* (1994) 143.