Crystal structure of the thortveitite-related M phase, $(Mn_xZn_{1-x})_2V_2O_7$, $(0.75 < x < 0.913)$: a combined synchrotron powder and single-crystal X-ray study

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Abstract

The determination of the crystal structure of the M phase, $(Mn_xZn_{1-x})_2V_2O_7$ $(0.75 < x < 0.913)$, in the pseudobinary $Mn_2V_2O_7$–$Zn_2V_2O_7$ system for $x \simeq 0.8$ shows that the previously published triclinic cell parameters for this thortveitite-related phase do not describe a true lattice for this phase. Instead, single-crystal X-ray data and Rietveld refinement of synchrotron X-ray powder data show that the M phase has a different triclinic structure in space group $P\bar{1}$ with $Z = 2$. As prior work has suggested, the crystal structure can be described as a distorted version of the thortveitite crystal structure of β-$Mn_2V_2O_7$. A two-fold superstructure in diffraction patterns of crystals of M phase used for single crystal X-ray diffraction work arises from twinning by reticular pseudo-merohedry. This superstructure can be described as a commensurate modulation of a pseudo-monoclinic basis structure closely related to the crystal structure of β-$Mn_2V_2O_7$. In comparison with the distortions introduced when β-$Mn_2V_2O_7$ transforms at low temperature to α-$Mn_2V_2O_7$, the distortions which give rise to the M phase from the β-$Mn_2V_2O_7$ prototype are noticeably less pronounced.

1. Introduction

Derivatives of the thortveitite structure ($Sc_2Si_2O_7$, space group type $C2/m$; Zachariasen, 1930; Cruickshank et $al.$, 1962; Foord et $al.$, 1993) with the general formula $M_2X_2O_7$ build up a rich structure family of considerable crystallo-chemical interest. Numerous representatives of this family have been described for disilicate, diphosphate, diarsenate and divanadate anions. Whereas the aristotype thortveitite crystal structure is structurally simple, many of the known hettotypes feature pronounced superstructures, and even incommensurately modulated structures, such as $Cr_2P_2O_7$ (Palatinus et $al.$, 2006) and $Zn_2P_2O_7$ (Stöger et $al.$, 2014). A number of these thortveitite-type phases are polymorphic, typically being isotypic with the thortveitite aristotype at high temperatures and transforming into one or more hettotypes at lower temperatures. Moreover, solid solutions increase the number of representatives of the thortveitite family. For example, the mineral petewilliamsite $((Ni,Co)_2As_2O_7)$ is reported (Roberts et $al.$, 2004) to crystallize in a structure different from those of the pure Ni end member and the pure Co end member (Weil & Stöger, 2010). In this regard, the $(Mn_xZn_{1-x})_2V_2O_7$ solid solution series, where the high temperature $Mn_2V_2O_7$ and $Zn_2V_2O_7$ end members have the aristotype thortveitite crystal structure, is of particular interest. Work by Zhuravlev et $al.$ (1993) and Krasnenko et $al.$ (2002) has shown that in the pseudobinary $Mn_2V_2O_7$–$Zn_2V_2O_7$ system there are two homogeneity ranges for phases referred to by Krasnenko et $al.$ (2002) as L and M phases, respectively. Zhuravlev et $al.$ (1993) reported lattice parameters for both these phases and suggested that the crystal structures of both these phases were related to that of thortveitite, but did not provide any other details such as lattice type, space group or atom positions within the unit cell.

A re-examination of the L phase by Rietveld analysis, inspired by the discovery of this phase as small precipitates in a family of zinc oxide varistors where small amounts of manganese oxide and vanadium oxide are added at levels of up to

2 mol% to the overall chemical composition of the powders from which the varistors are made, has shown that the *L* phase is a monoclinic threefold superstructure of the aristotype thortveitite crystal structure (Knowles *et al.*, 2009). This 2009 study also showed that the true unit cell was different from that reported earlier by Zhuravlev *et al.* (1993). In the light of this reassessment of the *L* phase, we have also synthesised the *M* phase both in form of polycrystalline and single crystalline material to determine its crystal structure and to examine how it is related to the aristotype thortveitite crystal structures of β-Mn$_2$V$_2$O$_7$ (Liao *et al.*, 1996) and β'-Zn$_2$V$_2$O$_7$ (Krasnenko *et al.*, 2003). The designation β' to denote this Zn$_2$V$_2$O$_7$ crystal structure was introduced by Krasnenko *et al.* (2003) to avoid confusion with an unconfirmed β-Zn$_2$V$_2$O$_7$ reported by Brown & Hummel (1965).

2. Results and discussion

The powder X-ray diffraction study of Zhuravlev *et al.* (1993) on Mn$_2$V$_2$O$_7$–M_2V$_2$O$_7$ binary systems for various divalent metal cations *M* showed that in the system Mn$_2$V$_2$O$_7$–Zn$_2$V$_2$O$_7$ a triclinic phase distinct from other phases occurred in the 65–85 mol% Mn$_2$V$_2$O$_7$ range. For a composition of 80 mol% Mn$_2$V$_2$O$_7$ – 20 mol% Zn$_2$V$_2$O$_7$ the lattice parameters quoted by Zhuravlev *et al.* (1993) are a = 6.606 (1) Å, b = 8.707 (1) Å, c = 4.999 (1) Å, α = 90.13 (2)°, β = 103.70 (2)° and γ = 90.43 (2)°. Subsequent work by Krasnenko *et al.* (2002) established the homogeneity range of 75 ($\pm$ 5) – 91.3 ($\pm$1.3) mol% Mn$_2$V$_2$O$_7$ at room temperature for this phase, which they designated the *M* phase. X-ray diffraction work by Krasnenko *et al.* (2002) using CuK_α radiation showed a characteristic X-ray diffraction signature of the *M* phase of two intense peaks at 27.6° and 29.5° 2θ. Krasnenko *et al.* (2002) also deduced from differential thermal analysis work that the *M* phase was a deformed version of the high temperature β-Zn$_2$V$_2$O$_7$ solid solution which dominates the pseudobinary Mn$_2$V$_2$O$_7$—Zn$_2$V$_2$O$_7$ phase diagram at high temperatures. The high temperature end-members of this Mn$_2$V$_2$O$_7$—Zn$_2$V$_2$O$_7$ system, *viz.* β-Mn$_2$V$_2$O$_7$ and β'-Zn$_2$V$_2$O$_7$, are isotypic (Liao *et al.*, 1996; Krasnenko *et al.*, 2003): both adopt the aristotype thortveitite crystal structure in space group type *C*2/*m* and *Z* = 2 (Zachariasen, 1930; Cruickshank *et al.*, 1962; Foord *et al.*, 1993). This crystal structure is characterised by a linear *X*–O–*X* angle between the two corner-sharing *X*O$_4$ tetrahedra of the *X*$_2$O$_7$ group, and with edge-sharing *M*O$_6$ octahedra of the cations. The *X*$_2$O$_7$ group is located on a site with symmetry 2/*m*. Since a *X*—O—*X* angle of 180° is highly unfavoured, the bridging O atom is usually considered disordered around the centre of inversion, as evidenced by a split position or large atomic displacement parameters. The unfavoured 180° *X*—O—*X* angle and the preference of different *M* cations for coordination polyhedra deviating from coordination number of six is responsible for the large amount of superstructures and incommensurately modulated structures that have been described for the thortveitite family.

2.1. Structural relationships

Preliminary analysis of our synchrotron radiation X-ray data using the unit cell lattice parameters suggested by Zhuralev *et al.* (1993) showed that all the strong reflections at low angles (< 34° 2θ) could be indexed with this unit cell, but that a number of weaker reflections could not be indexed. Furthermore, all the reflections which were indexed with this unit cell had $h + k$ even, implying a fit to a triclinic *C*-centred unit cell. Redefining the unit cell in terms of basis vectors $\mathbf{a}_2$, $\mathbf{b}_2$, $\mathbf{c}_2$ related to the basis vectors $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{c}_1$ defined by Zhuravlev *et al.* (1993) through the equations

$\mathbf{a}_2 = 0.5\ \mathbf{a}_1 + 0.5\ \mathbf{b}_1$

$\mathbf{b}_2 = -0.5\ \mathbf{a}_1 + 0.5\ \mathbf{b}_1$

$\mathbf{c}_2 = \mathbf{c}_1$

showed that some of the weaker reflections at low 2θ could now be indexed as integers hkl if the magnitudes of $\mathbf{b}_2$ and $\mathbf{c}_2$ were doubled to produce a new set of basis vectors $\mathbf{a}_3$, $\mathbf{b}_3$, $\mathbf{c}_3$. Refinement using $\mathbf{a}_3$, $\mathbf{b}_3$ and $\mathbf{c}_3$ showed that all the reflections attributable to the *M* phase, rather than attributable to the residual level of α-Mn$_2$V$_2$O$_7$ known to be present,

had $k + l$ even, implying that $\mathbf{a}_3$, $\mathbf{b}_3$ and $\mathbf{c}_3$ were consistent with a triclinic A-centred lattice. The set of basis vectors $\mathbf{a}_M$, $\mathbf{b}_M$, $\mathbf{c}_M$ produced to define a triclinic P lattice so that

$\mathbf{a}_M = 0.5\,\mathbf{b}_3 - 0.5\,\mathbf{c}_3$

$\mathbf{b}_M = 0.5\,\mathbf{b}_3 + 0.5\,\mathbf{c}_3$

$\mathbf{c}_M = \mathbf{a}_3$

were found to index all the M phase diffraction peaks satisfactorily. The basis vectors $\mathbf{a}_M$, $\mathbf{b}_M$, $\mathbf{c}_M$ are related to $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{c}_1$ through the equations

$\mathbf{a}_M = -0.5\,\mathbf{a}_1 + 0.5\,\mathbf{b}_1 - \mathbf{c}_1$

$\mathbf{b}_M = -0.5\,\mathbf{a}_1 + 0.5\,\mathbf{b}_1 + \mathbf{c}_1$

$\mathbf{c}_M = 0.5\,\mathbf{a}_1 + 0.5\,\mathbf{b}_1$

and, conversely,

$\mathbf{a}_1 = -0.5\,\mathbf{a}_M - 0.5\,\mathbf{b}_M + \mathbf{c}_M$

$\mathbf{b}_1 = 0.5\,\mathbf{a}_M + 0.5\,\mathbf{b}_M + \mathbf{c}_M$

$\mathbf{c}_1 = -0.5\,\mathbf{a}_M + 0.5\,\mathbf{b}_M$

A comparison of the indexing of low angle reflections in the synchrotron X-ray diffraction data to the triclinic unit cell defined by the basis vectors $\mathbf{a}_M$, $\mathbf{b}_M$ and $\mathbf{c}_M$ and to the unit cell defined by $\mathbf{a}_1$, $\mathbf{b}_1$ and $\mathbf{c}_1$ for the regions (a) 7–10°, (b) 10–13° and (c) 16–19° is shown in Fig. 1. The weaker peaks in these angular ranges cannot be indexed to the unit cell defined by $\mathbf{a}_1$, $\mathbf{b}_1$ and $\mathbf{c}_1$, but they can all be indexed to the triclinic unit cell defined by $\mathbf{a}_M$, $\mathbf{b}_M$ and $\mathbf{c}_M$.

To illustrate the relationship between the two basis vector sets, a clinographic projection of a block of $2 \times 2 \times 2$ unit cells defined by $\mathbf{a}_1$, $\mathbf{b}_1$ and $\mathbf{c}_1$ is shown in Fig. 2 outlined in blue. The unit cell of the M phase defined by $\mathbf{a}_M$, $\mathbf{b}_M$ and $\mathbf{c}_M$ is shown in red within this block. Lattice points of the M phase crystal structure defined by $\mathbf{a}_M$, $\mathbf{b}_M$ and $\mathbf{c}_M$ are shown as black dots. Fig. 2 is also useful in appreciating how the intermediate basis sets $\mathbf{a}_2$, $\mathbf{b}_2$, $\mathbf{c}_2$ and $\mathbf{a}_3$, $\mathbf{b}_3$, $\mathbf{c}_3$ used in this analysis of the X–ray diffraction data relate to $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{c}_1$ and $\mathbf{a}_M$, $\mathbf{b}_M$, $\mathbf{c}_M$.

Although the volume $\mathbf{a}_1 \cdot \mathbf{b}_1 \times \mathbf{c}_1$ of the unit cell defined by Zhuralev *et al.* (1993) and the volume $\mathbf{a}_M \cdot \mathbf{b}_M \times \mathbf{c}_M$ of the unit cell established here are the same, in the sense that the determinants of the metric tensors defined by these two basis sets have identical magnitudes, it is apparent that the vector set $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{c}_1$ does not describe an alternative description of the true unit cell. For example, relative to a lattice point at (0, 0, 0), positions within the unit cell such as (-½, ½, 0) reached by the vector $\mathbf{c}_1$ are not lattice points.

Rietveld refinement of the synchrotron X-ray powder pattern data shows that the M phase has a triclinic unit cell in space group $P\bar{1}$ with $Z = 2$, and with $a = 6.88143\,(1)$Å, $b = 7.92420\,(1)$ Å, $c = 5.45516\,(1)$ Å, $\alpha = 84.5309\,(1)°$, $\beta = 71.3730\,(1)°$ and $\gamma = 84.6100\,(1)°$. By comparison, the vectors $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{c}_1$ calculated from this refinement have magnitudes of 6.614 Å, 8.716 Å and 4.998 Å, with angles of 90.10°, 103.64° and 90.34° as effective values of α, β and γ, respectively.

2.2. Structure description

The room-temperature synchrotron powder diffraction study and the low-temperature single crystal X-ray diffraction study revealed very similar results in terms of structural details (bond lengths and bond angles). The main difference between the two structure refinements pertains to an additional disorder of the vanadium atoms in the single crystal model that was not evident in the synchrotron powder study. In the following description, only the major component of disorder is discussed. Relevant distances and angles for both components of disorder are collated in Table 1. The minor component of disorder found in the refinement of the single crystal data is designated in Table 1 by a prime character on

the vanadium ions. The principal building units of the M phase from the single crystal data are shown in Fig. 3.

The crystal structure of the M phase is a hettotype of the thortveitite aristotype and similar to that of α-$Mn_2V_2O_7$ (Liao *et al.*, 1996), but with almost identical α and γ values, rather than having α and γ values differing by 4.73°, and without the doubling of the c parameter which arises in α-$Mn_2V_2O_7$. Selected bond lengths and angles are given in Table 1 on the basis of both powder and single crystal data. The Mn^{2+} and Zn^{2+} cations within the structure randomly occupy their distorted octahedral sites (with an occupancy ratio Mn:Zn = 4:1 for $x = 0.2$). As noted above, the coordination behaviour of the M atoms plays a crucial role in the formation of complex superstructures of the thortveitite family. In the aristotype, one crystallographically unique M position is coordinated by four close O atoms and two more O atoms slightly further away. The resulting distorted MO_6 octahedra are connected via edges into sheets. These $^2_\infty[M_2O_6]$ sheets in the low-temperature $(Mn,Zn)_2V_2O_7$ hettotypes are characterized by an increased tendency to a 5-coordination of the metal cations with increasing Zn content: all cations in the Zn-rich L phase and half of the cations in the Mn-rich M phase are five-fold coordinated, while none are in the α-$Mn_2V_2O_7$ crystal structure. In comparison with the MnO_6 octahedra in β-$Mn_2V_2O_7$ (Liao *et al*., 1996), the MO_6 octahedra with mixed (Mn,Zn) occupancy in the M phase distort so that one (Mn/Zn)–O bond in each $(Mn/Zn)O_6$ octahedron is significantly larger than the other five, in a similar manner to the distortions which occur in α-$Mn_2V_2O_7$ when compared with β-$Mn_2V_2O_7$ (Liao *et al.*, 1996). The connectivity of the $(Mn/Zn)O_6$ octahedra is equivalent to the connectivity observed in the thortveitite aristotype.

The V_2O_7 divanadate groups have a modest degree of bending, so that V1–O1–V2 is about 163° in comparison with the two distinct groups of V–O–V bonds in α-$Mn_2V_2O_7$ with their bond angles of 174.3 (4)° and 133.2 (2)° (Liao *et al.*, 1996). The four V2–O distances in the $V2O_4$ tetrahedron remain tightly grouped in the range 1.67 – 1.74 Å, whereas the $V1O_4$ tetrahedron is significantly more distorted, in a similar way to one of the four vanadium oxygen tetrahedra in α-$Mn_2V_2O_7$ (Liao *et al.*, 1996). Owing to the more flexible coordination chemistry of vanadium compared to Si, P or As, in some low-temperature $(Mn,Zn)V_2O_7$ phases adjacent V_2O_7 groups are connected to linear V_4O_{14} tetravanadates featuring VO_{4+1} or VO_{2+3} coordination polyhedra: in the L (Knowles *et al.*, 2009) and the M phases VO_4 tetrahedra of adjacent V_2O_7 groups are additionally connected via apical O atoms resulting in a pair of distorted VO_5 trigonal bipyramids connected by an edge. In the L phase the bipyramids feature two close O atoms (1.630 (8) Å) and three more O atoms slightly further away (1.887 (10) – 2.028 (10) Å), whereas the M phase features a distinct [4+1] coordination (short bonds: $\simeq$ 1.65 – 1.82 Å; long bond: $\simeq$ 2.22 Å). The pair of VO_5 trigonal bipyramids is connected on each side to a VO_4 tetrahedron via a corner to form a V_4O_{14} tetramer. In the L phase half of all of the V_2O_7 units are joined to V_4O_{14} tetramers, while in the M phase all of these V_2O_7 units are joined to V_4O_{14} tetramers.

It is of interest to compare the overall displacement of atom positions in the M phase and α-$Mn_2V_2O_7$ relative to the atom positions in the high temperature divanadate phase. Liao *et al.* (1996) defined a pseudo-monoclinic setting which they termed α'-$Mn_2V_2O_7$ with a = 6.905Å, b = 8.603 Å, c = 4.939 Å, α = 88.91°, β = 105.36° and γ = 88.91°; this is equivalent to the pseudo-monoclinic setting for the M phase defined by Zhuravlev *et al.* (1993), but with the directions of the x- and z-axes interchanged, so that α and γ are acute, rather than obtuse. The shifts of atoms in α'-$Mn_2V_2O_7$ relative to their positions in β-$Mn_2V_2O_7$ shown in Table 11 of Liao *et al.* (1996) are defined within this pseudo-monoclinic setting. The calculated shifts of atoms in α'-$Mn_2V_2O_7$ relative to their positions in β-$Mn_2V_2O_7$ are extremely similar (all within 3%) when determined in the monoclinic β-$Mn_2V_2O_7$ setting; this latter setting is evidently more suitable a reference unit cell for making comparisons of atom shifts with those in the M phase. It is also evident that the choice of the pseudo-monoclinic setting in which M atomic positions are defined can be either with respect to the pseudo-monoclinic setting of Liao *et al*. (1996) or Zhuravlev *et al.* (1993); we have chosen the latter.

Hence, to make a comparison with atom shifts in α'-Mn$_2$V$_2$O$_7$ relative to β-Mn$_2$V$_2$O$_7$, we have defined the pseudo-monoclinic setting with basis vectors $\mathbf{a}_{M'}$, $\mathbf{b}_{M'}$, $\mathbf{c}_{M'}$ so that

$\mathbf{a}_{M'} = -0.5\,\mathbf{a}_M - 0.5\,\mathbf{b}_M + \mathbf{c}_M$

$\mathbf{b}_{M'} = 0.5\,\mathbf{a}_M + 0.5\,\mathbf{b}_M + \mathbf{c}_M$

$\mathbf{c}_{M'} = -0.5\,\mathbf{a}_M + 0.5\,\mathbf{b}_M$

i.e., the basis vectors $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{c}_1$ defined by Zhuravlev *et al.* (1993), re-designated $\mathbf{a}_{M'}$, $\mathbf{b}_{M'}$, $\mathbf{c}_{M'}$ to emphasise that these are not basis vectors of a unit cell. Atoms at positions $(x,y,z)_M$ with respect to the coordinate system of the M phase setting transform into positions $(X,Y,Z)_{M'}$, where

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix}_{M'} = \begin{pmatrix} -0.5 & -0.5 & 0.5 \\ 0.5 & 0.5 & 0.5 \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_M$$

using conventional algebra for the transformation of indices following a change of unit cell (Kelly & Knowles, 2012). To make a direct comparison with the atom positions in β-Mn$_2$V$_2$O$_7$ and, by implication, atom positions in the high temperature solid solution β-(Mn,Zn)$_2$V$_2$O$_7$, the atom positions defined with respect to the M basis have first to be redefined with respect to an origin at $(-0.25, -0.25, 0)$; these then produce atom positions which are defined with respect to the M' basis, after which translations of $(\pm0.5, \pm0.5, 0)$ have to be applied to some of the atom positions to be to able to compare with the atom positions defined in β-Mn$_2$V$_2$O$_7$ and to take account of the C-centring present in β-Mn$_2$V$_2$O$_7$. The final atom positions with respect to the M' basis with which to compare the equivalent positions in β-Mn$_2$V$_2$O$_7$ and the calculated atom shifts are shown in Table 2. It is evident that the atom shifts are all very small – the average magnitude of shift of the eleven atoms in Table 2 is 0.14 Å. The bridging O1 oxygen atom in the V1–O1–V2 divanadate group linkage is subjected to the most movement: 0.33 Å.

By comparison, the deviations of atoms in α-Mn$_2$V$_2$O$_7$ relative to their positions in β-Mn$_2$V$_2$O$_7$ are more significant, with some oxygen atoms deviating by more than 1 Å and half the vanadium atoms by more than 0.4 Å (Table 11 of Liao *et al.*, 1996). The deviations of the (Mn,Zn)O$_6$ octahedra and VO$_4$ tetrahedra can be appreciated graphically in representations of the crystal structures of β-Mn$_2$V$_2$O$_7$, M phase and α-Mn$_2$V$_2$O$_7$ in similar orientations, as shown in Figs 4–6. Finally, since the first coordination spheres in β-(Mn,Zn)$_2$V$_2$O$_7$ are all distorted, and bonds are not broken in the phase transitions on cooling to the lower symmetry α-Mn$_2$V$_2$O$_7$ and M phases, it is evident that both these phase transitions exhibit behaviour consistent with displacive phase transitions, rather than with reconstructive phase transitions (Putnis, 1992).

2.3. Twinning

The point groups of the β-Mn$_2$V$_2$O$_7$ ($2/m$) aristotype and the M phase ($\bar{1}$) are related by a group/subgroup relationship of index 2. Accordingly, crystals of the M phase can be twins composed of two individuals. The twin law relating the individuals is derived by coset decomposition of $\bar{1}$ in $2/m$: { $m_{(010)}$, $2_{[010]}$ }, where the indices are given with respect to the monoclinic aristotype unit cell. Hence, with respect to the monoclinic aristotype unit cell, twinning occurs by reflection in the (010) plane. In the setting used in Section 2.2 to describe the crystal structure of the M phase, twinning occurs in the M phase by reflection in the (111) plane: this (111) plane has an interplanar spacing the same as the (020) interplanar spacing in the monoclinic aristotype to within 0.1%.

The twofold superstructure of the M phase can be described as a commensurate modulation of a pseudo-monoclinic basic structure closely related to β-Mn$_2$V$_2$O$_7$ with the modulation wave vector $\mathbf{q} = (\mathbf{a}^* + \mathbf{b}^*)/2$ with respect to the reciprocal basis of β-Mn$_2$V$_2$O$_7$. Therefore, twinning is by reticular pseudo-merohedry (Nespolo, 2015). One out of two reflections of the two individuals overlap approximately, whereas the remaining reflections are clearly separated. At

higher diffraction angles, a distinct splitting of the overlapping reflections is observed arising to a deviation from perfectly monoclinic metrics.

3. Experimental

3.1. Polycrystalline material

High purity powders of ZnO (Aldrich), V_2O_5 (Aldrich) and MnO (Aldrich) were used for the preparation of α-$Zn_2V_2O_7$ and α-$Mn_2V_2O_7$ powders as described elsewhere for the L phase (Knowles *et al.*, 2009). Powders of the appropriate chemical compositions were pressed into pellets and sintered either at 873 K for 48 h or 1073 K for 24 h on alumina substrates to achieve chemical homogeneity, subsequently confirmed by X-ray diffraction of powders produced from the crushed pellets. For the M phase work a target composition of 0.8 $Mn_2V_2O_7$ – 0.2 $Zn_2V_2O_7$ was selected on the basis of the phase diagram work of Krasnenko *et al.* (2002) through the mixing together of appropriate quantities of the α-$Mn_2V_2O_7$ and α-$Zn_2V_2O_7$ powders. Powders were pressed into pellets and then sintered initially at 873–923 K for 24 h on alumina substrates, after which they were reground into a powder. Repeated sintering and regrinding operations were carried out subsequently at 1023 K for periods of 48 and 72 h to attempt to achieve a powder of a single composition. Despite this repeated sintering and regrinding, the final powder for detailed structural analysis contained a residual level of α-$Mn_2V_2O_7$, identified by the presence in the synchrotron X-ray diffraction pattern of faint reflections from the three strongest (202), (022) and (02$\bar{2}$) α-$Mn_2V_2O_7$ reflections at 2θ values of 14.699°, 15.053° and 15.088°, the latter two reflections in a region of the diffraction pattern where there were no diffraction peaks from M phase (see supplementary Figs. 1 and 2).

3.2. Single crystalline material

0.7134 g (6.10 mmol) NH_4VO_3, 0.3410 g (4.81 mmol) MnO and 0.099 g (1.22 mmol) ZnO were mixed and ground in an agate mortar, transferred into a platinum crucible and heated in succession for 2 h at 1190, 970, 770 and 570 K with 12 h cooling time between each temperature step. Finally, the crucible was cooled to room temperature over 12 h. Tiny black crystals of the M phase with undefined crystal forms were isolated from the reaction mixture.

3.3. Refinement

Crystal data, details of data collection and structure refinements are summarized in Table 3. A cyclic permutation of $\mathbf{a}_1$, $\mathbf{b}_1$ and $\mathbf{c}_1$ in Table 3 produces a description of the unit cell as a Niggli reduced unit cell (Niggli, 1928) satisfying the condition $|\mathbf{a}_1| < |\mathbf{b}_1| < |\mathbf{c}_1|$ with its three angular parameters all being less than 90°. This can be confirmed straightforwardly using the algorithm proposed by Křivý and Gruber (1976). In common with the crystal structure refinement of the L phase (Knowles *et al.*, 2009), the atom positions within the high-temperature $C2/m$ β-$Mn_2V_2O_7$ thortveitite-type phase specified by Liao *et al.* (1996) were used to define positions of atoms within the M phase with respect to the M phase basis vectors. A shift of the origin of the M-phase unit cell by [0.25, 0.25, 0] enabled these atom positions to be reduced to subgroups of initial atom positions for structure refinement consistent with a centre of symmetry at the origin of the M phase structure. Structure refinement was then easily achieved with random occupation of the octahedral atom sites by Mn and Zn atoms. No advantage in refinement was found from lowering the space group symmetry to $P1$. In the synchrotron powder pattern the (202) reflection from α-$Mn_2V_2O_7$ appeared as a distinct minor shoulder of a more intense (021) M phase reflection and could not be excluded in the Rietveld analysis, whereas the (022) and (02$\bar{2}$) α-$Mn_2V_2O_7$ reflections were able to be excluded in order to optimise the Rietveld analysis, as were other even more minor peaks at low 2θ clearly not attributable to the M phase.

Single crystal data were integrated with SAINT-Plus (Bruker, 2016) as twins with partial reflection overlap (HKLF5-style intensity data) and corrections for absorption effects were applied using the multi-scan method implemented in TWINABS (Bruker, 2016). Structure refinements based on an initial model derived from powder data were performed using the Jana2006 software package (Petříček *et al.*, 2014). Excess electron density in difference Fourier maps was attributed to a disorder of the divanadate group. An attempt of placing overlapping and non-overlapping reflections on different scale factors did not resolve the disorder.

Table 1

Selected bond lengths and angles (Å, °)

	Powder data	Single crystal data
(Mn/Zn)1—O5[i]	2.107 (2)	2.100 (4)
(Mn/Zn)1—O6[ii]	2.111 (2)	2.099 (3)
(Mn/Zn)1—O3[iii]	2.143 (2)	2.119 (3)
(Mn/Zn)1—O2	2.187 (2)	2.157 (3)
(Mn/Zn)1—O5[iv]	2.242 (2)	2.229 (4)
(Mn/Zn)1—O7	2.538 (2)	2.474 (4)
(Mn/Zn)2—O4	2.082 (2)	2.059 (4)
(Mn/Zn)2—O7[ii]	2.097 (2)	2.098 (4)
(Mn/Zn)2—O3	2.156 (2)	2.145 (3)
(Mn/Zn)2—O2[iii]	2.165 (2)	2.121 (3)
(Mn/Zn)2—O6	2.216 (2)	2.198 (4)
(Mn/Zn)2—O4[iii]	2.328 (2)	2.371 (4)
V1—O7[ii]	1.636 (2)	1.664 (5)
V1—O4[ii]	1.679 (3)	1.674 (5)
V1—O1[ii]	1.785 (2)	1.822 (2)
V1—O3[v]	1.801 (2)	1.776 (2)
V1—O3[vi]	2.209 (2)	2.234 (3)
V1'—O7[ii]	-	1.594 (8)
V1'—O4[ii]	-	1.749 (9)
V1'—O1[ii]	-	1.570 (6)
V1'—O3[v]	-	1.960 (5)
V2—O2[ii]	1.674 (2)	1.734 (2)
V2—O6[vii]	1.684 (2)	1.693 (4)
V2—O5[ii]	1.692 (3)	1.719 (5)
V2—O1	1.737 (2)	1.683 (2)
V2'—O2[ii]	-	1.611 (5)
V2'—O6[vii]	-	1.724 (8)
V2'—O5[ii]	-	1.621 (9)
V2'—O1	-	1.983 (7)
V2—O1—V1[ii]	162.74 (11)	165.08 (13)
V2—O1—V1'[ii]	-	159.2 (2)
V2'—O1—V1'[ii]	-	156.9 (3)
V2'—O1—V1[ii]	-	163.00 (19)

Symmetry codes: (i) x-1, y, z; (ii) -x+1, -y+1, -z+1; (iii) -x+1, -y+1, -z+2; (iv) -x+1, -y, -z+2; (v) -x+2, -y+1, -z+1; (vi) x, y, z-1; (vii) -x+1, -y+2, -z+1.

Table 2

Comparison of atomic positions in the *M* phase (derived from the powder synchrotron refinement), represented in a pseudo-monoclinic unit cell, *M′*, defined by Zhuravlev *et al.* (1993), and their corresponding positions in β-$Mn_2V_2O_7$ representing the more general β-$(Mn,Zn)_2V_2O_7$ high temperature solid solution.

Atom (*M′*)	Atom (β)	$x(M')$	$y(M')$	$z(M')$	$x(\beta)$	$y(\beta)$	$z(\beta)$	Δx	Δy	Δz	Shift (Å)
(Mn/Zn)1	Mn	0.0044	0.8102	–0.0145	0.0	0.8109	0.0	–0.0044	0.0007	0.0145	0.084
(Mn/Zn)2	Mn	0.0011	0.8177	0.0117	0.0	0.8109	0.0	–0.0011	–0.0068	–0.0117	0.082
V1	V	0.7551	0.0011	0.3982	0.7341	0.0	0.4032	–0.0210	–0.0011	0.0050	0.149
V2	V	0.7126	–0.0023	0.3962	0.7341	0.0	0.4032	0.0215	0.0023	0.0070	0.142
O1	O1	0.5386	0.0055	0.5542	0.5	0.0	0.5	–0.0386	–0.0055	–0.0542	0.330
O2	O2	0.8826	–0.0029	0.7031	0.9093	0.0	0.7191	0.0267	0.0029	0.0160	0.180
O3	O2	0.9447	0.0049	0.7227	0.9093	0.0	0.7191	–0.0354	–0.0049	–0.0036	0.238
O4	O3	0.7231	0.1593	0.2019	0.7322	0.1614	0.2123	0.0091	0.0021	0.0104	0.072
O5	O3	0.7271	0.1585	0.2121	0.7322	0.1614	0.2123	0.0051	0.0029	0.0002	0.043
O6	O3	0.7366	0.1598	0.2107	0.7322	0.1614	0.2123	–0.0044	0.0016	0.0016	0.036
O7	O3	0.7073	0.1590	0.2226	0.7322	0.1614	0.2123	0.0249	0.0024	–0.0103	0.187

Note: The components Δx, Δy and Δz of the shifts and the magnitudes of the shifts are all defined with respect to the β-$Mn_2V_2O_7$ set of basis vectors quoted by Liao *et al.* (1996).

Table 3

Experimental details

	(powder)	(sc)
Crystal data		
Chemical formula	$Mn_{1.60}O_7V_2Zn_{0.40}$	$Mn_{1.612}O_7V_2Zn_{0.388}$
M_r	327.94	327.8
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	298	100
a, b, c (Å)	6.88143 (1), 7.92420 (1), 5.45516 (1)	6.8575 (2), 7.9147 (3), 5.4505 (6)
α, β, γ (°)	84.5309 (1), 71.3730 (1), 84.6100 (1)	84.6178 (17), 71.450 (2), 84.719 (2)
V (Å^3)	279.97 (1)	278.61 (3)
Z	2	2
Radiation type	Synchrotron, $\lambda = 0.826406$ Å	Mo $K\alpha$
μ (mm^{-1})	12.81	8.45
Specimen shape, size (mm)	Cylinder, 40 × 0.5	0.06 × 0.05 × 0.04
Data collection		
Diffractometer	Beamline I11, Diamond Light Source	Bruker *KAPPA APEX* II CCD
Specimen mounting	Borosilicate glass capillary	–
Data collection mode	Transmission	–
Data collection method	Continuous	ω– and φ–scans
Absorption correction	–	Multi-scan (*TWINABS*; Bruker, 2016)
T_{min}, T_{max}	–	0.60, 0.71
No. of measured, independent and observed reflections	–	4889, 4889, 3222
R_{int}	–	0

θ values (°)	$2\theta_{min} = 5.5$ $2\theta_{max} = 151.75$ $2\theta_{step} = 0.001$	$\theta_{max} = 43.3$, $\theta_{min} = 3.1$
Distance from source to specimen (mm)	–	0.965
Refinement		
R factors and goodness of fit	$R_p = 0.086$, $R_{wp} = 0.111$, $R_{exp} = 0.068$, $R_{Bragg} = 0.086$, $\chi^2 = 1.638$	$R[F > 3\sigma(F)] = 0.042$, $wR(F) = 0.102$, $S = 1.18$
No. of parameters	60	–
No. of restraints	6	110
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	–	0.033

Computer programs: *APEX3* (Bruker, 2016), *SAINT-Plus* (Bruker, 2016), SHELXT (Sheldrick, 2015), Bruker AXS TOPAS4.2 (Coelho, 2009), JANA-2006 (Petříček *et al.*, 2014), *CrystalMaker* (Palmer, 2014), *publCIF* (Westrip, 2010).

References

Brown, J. J. & Hummel, F. A. (1965). *Trans. Brit. Ceram. Soc.* **64**, 419–437.

Bruker (2016). *APEX3*, *SAINT*-Plus and *TWINABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Coelho, A. A. (2009). *TOPAS User's Manual*. Version 4.2. Bruker AXS GmbH, Karlsruhe, Germany.

Cruickshank, D. W. J., Lynton, H. & Barclay, G. A. (1962). *Acta Cryst.* **15**, 491–498.

Foord, E. E., Birmingham, S. D., Demartin, F., Pilati, T., Gramaccioli, C. M. & Lichte, F. (1993). *Can. Mineral.* **31**, 337–346.

Kelly, A. & Knowles, K. M. (2012). *Crystallography and Crystal Defects*, Second Edition, Appendix 4. Chichester, U. K.: John Wiley & Sons Ltd.

Knowles, K. M., Vickers, M. E., Sil, A., Han, Y.-H. & Jaffrenou, P. (2009). *Acta Cryst.* B**65**, 160–166.

Krasnenko, T. I., Rotermel, M. V., Zolotukhina, L. V., Maksimova, L. G. & Zakharov, R. G. (2002). *Zh. Neorg. Khim.* **47**, 1888–1891 *Russ. J. Inorg. Chem. (Engl. Transl.)* **47**, 1737–1740.

Krasnenko, T. I., Zubkov, V. G., Tyutyunnik, A. P., Zolotukhina, L. V. & Vasyutinskaya, E. F. (2003). *Kristallografiya*, **48**, 40–43 *Crystallography Reports (Engl. Trans.)* **48**, 35–38.

Křivý, I. & Gruber, B. (1976). *Acta Cryst.* A**32**, 297–298.

Liao, J.-H., Leroux, F., Payen, C., Guyomard, D. & Piffard, Y. (1996). *J. Solid State Chem.* **121**, 214–224.

Nespolo, M. (2015). *Cryst Res. Technol.* **50**, 362–371.

Niggli, P. (1928). *Handbuch der Experimentalphysik*, Vol. 7, Part 1: *Krystallographische und Strukturtheoretische Grundbegriffe*, Chapter 4, §1. Leipzig, Germany: Akademische Verlagsgesellschaft m. b. H.

Palatinus, L., Dušek, M., Glaum, R. & El Bali, B. (2006). *Acta Cryst.* B**62**, 556–566.

Palmer, D. C. (2014). *CrystalMaker*. CrystalMaker Software Ltd, Begbroke, Oxfordshire, England.

Petříček, V., Dušek, M. & Palatinus, L. (2014). *Z. Kristallogr.* **229**, 345–352.

Putnis, A. (1992). *Introduction to Mineral Sciences*, Chapter 12, Cambridge, U. K: Cambridge University Press.

Roberts, A. C., Burns, P. C., Gault, R. A., Criddle, A. J. & Feinglos, M. N. (2004). *Mineral. Mag.* **68**, 231–240.

Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.

Stöger, B., Weil, M. & Dušek, M. (2014). *Acta Cryst.* B**70**, 539–554.

Tang, C. C., Thompson, S. P., Hill, T. P., Wilkin, G. R. & Wagner, U. H. (2007). *Z. Kristallogr. Suppl.* **26**, 153–158.

Thompson, S. P., Parker, J. E., Potter, J., Hill, T. P., Birt, A., Cobb, T. M., Yuan, F. & Tang, C. C. (2009). *Rev. Sci. Instrum.* **80**, 075107-1–075107-9.

Weil, M. & Stöger, B. (2010). *Acta Cryst.* B**66**, 603–614.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zachariasen, W. H. (1930). *Z. Kristallogr.* **73**, 1–6.

Zhuravlev, V. D., Velikodnyi, Yu. A. & Surat, L. L. (1993). *Zh. Neorg. Khim.* **38**, 1221–1224 *Russ. J. Inorg. Chem. (Engl. Transl.)* **38**, 1133–1136.

Figure 1

A comparison of the indexing of low angle reflections in the synchrotron X-ray diffraction data to the triclinic unit cell determined in this paper and to the unit cell determined by Zhuravlev *et al.* (1993) for the regions (a) 7–10°, (b) 10–13° and (c) 16–19°. Indexing according to the unit cell of Zhuravlev *et al.* is shown in italicised bold; each indexed reflection has $h + k$ even. It is evident that the weaker reflections in these angular ranges cannot be indexed to the unit cell determined by Zhuravlev *et al.*, but that they can all be indexed to the triclinic unit cell determined in this paper.

Figure 2

Clinographic projection of a block of $2 \times 2 \times 2$ unit cells for the M phase proposed by Zhuravlev *et al.* (1993) outlined in blue. The unit cell of the M phase determined in this paper is shown in red within this block. Lattice points of the M phase crystal structure are shown as black dots. It is evident from the three-dimensional periodicity of these lattice points that the unit cell proposed by Zhuravlev *et al.* is not an alternative unit cell description for the M phase.

Figure 3

The principal building units in the crystal structure of the M phase with displacement ellipsoids drawn at the 74% probability level from the single crystal data. The major component of the disordered vanadium sites within the divanadate group with an occupancy fraction of 0.843 is indicated with black bonds, and the minor component with an occupancy fraction of 0.157 is indicated with yellow bonds. Symmetry codes adjacent to atoms shown as superscripts refer to those specified in the footnote of Table 1.

Figure 4

A comparison of the crystal structures of β-$Mn_2V_2O_7$, the M phase and a-$Mn_2V_2O_7$ viewed along the crystallographically equivalent directions (*a*) $[00\bar{1}]_\beta$, (*b*) $[\bar{1}10]_M$ and (*c*) $[\bar{1}10]_\alpha$. Octahedra containing either Mn for β-$Mn_2V_2O_7$ and α-

$Mn_2V_2O_7$ or Mn and Zn for M phase are in light blue, while tetrahedra containing V are in green. A projection of the unit cell is outlined in black in each graphical representation.

Figure 5

A comparison of the crystal structures of β-$Mn_2V_2O_7$, the M phase and α-$Mn_2V_2O_7$ viewed along the crystallographically equivalent directions (a) $[0\bar{1}0]_\beta$, (b) $[\bar{1}\bar{1}2]_M$ and (c) $[\bar{1}\bar{1}1]_\alpha$. The colour scheme is the same as Fig. 4. A projection of the β-$Mn_2V_2O_7$ unit cell is outlined in black in (a).

Figure 6

A comparison of the crystal structures of β-$Mn_2V_2O_7$, the M phase and α-$Mn_2V_2O_7$ viewed along the crystallographically equivalent directions (a) $[\bar{1}00]_\beta$, (b) $[\bar{1}\bar{1}2]_M$ and (c) $[\bar{1}\bar{1}1]_\alpha$. The colour scheme is the same as Fig. 4. A projection of the β-$Mn_2V_2O_7$ unit cell is outlined in black in (a).

supporting information

Crystal structure of the thortveitite-related *M* phase, (Mn$_x$Zn$_{1-x}$)$_2$V$_2$O$_7$, (0.75 < *x* < 0.913): a combined synchrotron powder and single-crystal X-ray study

Kevin M. Knowles,* Anjan Sil, Berthold Stöger and Matthias Weil

Computing details

Data collection: *APEX3* (Bruker, 2016) for sc. Cell refinement: *SAINT-Plus* (Bruker, 2016) for sc. Data reduction: *SAINT-Plus* (Bruker, 2016) for sc. Program(s) used to solve structure: SHELXT (Sheldrick, 2015) for sc. Program(s) used to refine structure: Bruker AXS TOPAS4.2 (Coelho, 2009) for powder; JANA-2006 (Petříček *et al.*, 2014) for sc. For both compounds, molecular graphics: *CrystalMaker* (Palmer, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(powder) Manganese zinc divanadate, Mn$_{1.6}$Zn$_{0.4}$V$_2$O$_7$

Crystal data

Mn$_{1.60}$O$_7$V$_2$Zn$_{0.40}$	γ = 84.6100 (1)°
M_r = 327.94	V = 279.97 (1) Å^3
Triclinic, $P\bar{1}$	Z = 2
Hall symbol: -p 1	D_x = 3.89 Mg m^{-3}
a = 6.88143 (1) Å	Synchrotron radiation, λ = 0.826406 Å
b = 7.92420 (1) Å	μ = 12.81 mm^{-1}
c = 5.45516 (1) Å	T = 298 K
α = 84.5309 (1)°	dark grey
β = 71.3730 (1)°	cylinder, 40 × 0.5 mm

Data collection

Beamline I11, Diamond Light Source diffractometer	Data collection mode: transmission
	Scan method: continuous
Specimen mounting: Borosilicate glass capillary	$2\theta_{min}$ = 5.5°, $2\theta_{max}$ = 151.75°, $2\theta_{step}$ = 0.001°

Refinement

R_p = 0.086	6 restraints
R_{wp} = 0.111	$(\Delta/\sigma)_{max}$ = 0.001
R_{exp} = 0.068	Background function: Chebychev polynomial,
R_{Bragg} = 0.086	Coefficient 0 64.55935 1 -48.25469 2 31.42671 3
Excluded region(s): 14.9-15.2, 19.25-19.35,	-21.91713 4 15.57408 5 -10.13776 6 5.686649 7
28.55-28.86, 28.925-29.05 degrees	-2.320198 8 -1.271288 9 1.725147 10 -3.066357
60 parameters	

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.16013 (8)	0.14568 (6)	0.81455 (9)	0.0096 (1)	0.8
Zn1	0.16013 (8)	0.14568 (6)	0.81455 (9)	0.0096 (1)	0.2
Mn2	0.65244 (7)	0.66416 (6)	0.81888 (9)	0.0096 (1)	0.8
Zn2	0.65244 (7)	0.66416 (6)	0.81888 (9)	0.0096 (1)	0.2
V1	0.82609 (7)	0.42791 (6)	0.24385 (9)	0.0038 (1)	

V2	0.30553 (8)	0.90932 (6)	0.28968 (9)	0.0038 (1)
O1	0.2064 (3)	0.7606 (3)	0.5441 (4)	0.0136 (1)
O2	0.4557 (3)	0.1588 (2)	0.8797 (4)	0.0136 (1)
O3	0.9188 (3)	0.6415 (2)	0.9496 (4)	0.0136 (1)
O4	0.3671 (3)	0.5691 (3)	0.8824 (4)	0.0136 (1)
O5	0.8597 (3)	0.0718 (3)	0.8855 (4)	0.0136 (1)
O6	0.6965 (4)	0.9072 (3)	0.5769 (4)	0.0136 (1)
O7	0.2056 (3)	0.4281 (3)	0.5483 (4)	0.0136 (1)

Geometric parameters (Å, º) for (powder)

Mn1—O5[i]	2.107 (2)	Mn2—O4[iii]	2.328 (2)
Mn1—O6[ii]	2.111 (2)	Zn2—O4	2.082 (2)
Mn1—O3[iii]	2.143 (2)	Zn2—O7[ii]	2.097 (2)
Mn1—O2	2.187 (2)	Zn2—O3	2.156 (2)
Mn1—O5[iv]	2.242 (2)	Zn2—O2[iii]	2.165 (2)
Mn1—O7	2.538 (2)	Zn2—O6	2.216 (2)
Zn1—O5[i]	2.107 (2)	Zn2—O4[iii]	2.328 (2)
Zn1—O6[ii]	2.111 (2)	V1—O7[ii]	1.636 (2)
Zn1—O3[iii]	2.143 (2)	V1—O4[ii]	1.679 (3)
Zn1—O2	2.187 (2)	V1—O1[ii]	1.785 (2)
Zn1—O5[iv]	2.242 (2)	V1—O3[v]	1.801 (2)
Zn1—O7	2.538 (2)	V1—O3[vi]	2.209 (2)
Mn2—O4	2.082 (2)	V2—O2[ii]	1.674 (2)
Mn2—O7[ii]	2.097 (2)	V2—O6[vii]	1.684 (2)
Mn2—O3	2.156 (2)	V2—O5[ii]	1.692 (3)
Mn2—O2[iii]	2.165 (2)	V2—O1	1.737 (2)
Mn2—O6	2.216 (2)		
O5[i]—Mn1—O6[ii]	102.45 (9)	O7[ii]—Mn2—O6	80.00 (7)
O5[i]—Mn1—O3[iii]	97.53 (8)	O7[ii]—Mn2—O4[iii]	106.30 (7)
O5[i]—Mn1—O2	157.57 (8)	O3—Mn2—O2[iii]	81.75 (8)
O5[i]—Mn1—O5[iv]	77.60 (10)	O3—Mn2—O6	101.54 (8)
O5[i]—Mn1—O7	109.79 (8)	O3—Mn2—O4[iii]	70.19 (8)
O6[ii]—Mn1—O3[iii]	139.34 (7)	O2[iii]—Mn2—O6	80.30 (7)
O6[ii]—Mn1—O2	92.18 (8)	O2[iii]—Mn2—O4[iii]	92.63 (7)
O6[ii]—Mn1—O5[iv]	117.25 (8)	O6—Mn2—O4[iii]	169.97 (9)
O6[ii]—Mn1—O7	72.62 (7)	O4—Zn2—O7[ii]	96.73 (9)
O3[iii]—Mn1—O2	81.54 (8)	O4—Zn2—O3	143.61 (8)
O3[iii]—Mn1—O5[iv]	101.38 (8)	O4—Zn2—O2[iii]	95.31 (8)
O3[iii]—Mn1—O7	67.36 (7)	O4—Zn2—O6	113.77 (9)
O2—Mn1—O5[iv]	80.61 (8)	O4—Zn2—O4[iii]	73.75 (10)
O2—Mn1—O7	90.66 (7)	O7[ii]—Zn2—O3	97.79 (8)
O5[iv]—Mn1—O7	166.84 (8)	O7[ii]—Zn2—O2[iii]	159.79 (7)
O5[i]—Zn1—O6[ii]	102.45 (9)	O7[ii]—Zn2—O6	80.00 (7)
O5[i]—Zn1—O3[iii]	97.53 (8)	O7[ii]—Zn2—O4[iii]	106.30 (7)
O5[i]—Zn1—O2	157.57 (8)	O3—Zn2—O2[iii]	81.75 (8)
O5[i]—Zn1—O5[iv]	77.60 (10)	O3—Zn2—O6	101.54 (8)
O5[i]—Zn1—O7	109.79 (8)	O3—Zn2—O4[iii]	70.19 (8)
O6[ii]—Zn1—O3[iii]	139.34 (7)	O2[iii]—Zn2—O6	80.30 (7)
O6[ii]—Zn1—O2	92.18 (8)	O2[iii]—Zn2—O4[iii]	92.63 (7)

O6[ii]—Zn1—O5[iv]	117.25 (8)	O6—Zn2—O4[iii]	169.97 (9)
O6[ii]—Zn1—O7	72.62 (7)	O7[ii]—V1—O4[ii]	113.90 (11)
O3[iii]—Zn1—O2	81.54 (8)	O7[ii]—V1—O1[ii]	100.52 (10)
O3[iii]—Zn1—O5[iv]	101.38 (8)	O7[ii]—V1—O3[v]	119.95 (11)
O3[iii]—Zn1—O7	67.36 (7)	O4[ii]—V1—O1[ii]	103.33 (10)
O2—Zn1—O5[iv]	80.61 (8)	O4[ii]—V1—O3[v]	118.72 (10)
O2—Zn1—O7	90.66 (7)	O1[ii]—V1—O3[v]	93.80 (8)
O5[iv]—Zn1—O7	166.84 (8)	O2[ii]—V2—O6[vii]	111.52 (11)
O4—Mn2—O7[ii]	96.73 (9)	O2[ii]—V2—O5[ii]	113.18 (10)
O4—Mn2—O3	143.61 (8)	O2[ii]—V2—O1	109.11 (9)
O4—Mn2—O2[iii]	95.31 (8)	O6[vii]—V2—O5[ii]	110.53 (11)
O4—Mn2—O6	113.77 (9)	O6[vii]—V2—O1	106.70 (10)
O4—Mn2—O4[iii]	73.75 (10)	O5[ii]—V2—O1	105.39 (10)
O7[ii]—Mn2—O3	97.79 (8)	V2—O1—V1[ii]	162.74 (11)
O7[ii]—Mn2—O2[iii]	159.79 (7)		

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y, -z+2$; (v) $-x+2, -y+1, -z+1$; (vi) $x, y, z-1$; (vii) $-x+1, -y+2, -z+1$.

(sc)

Crystal data

$Mn_{1.612}O_7V_2Zn_{0.388}$	$Z = 2$
$M_r = 327.8$	$F(000) = 308$
Triclinic, $P\bar{1}$	$D_x = 3.907$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
$a = 6.8575$ (2) Å	Cell parameters from 1679 reflections
$b = 7.9147$ (3) Å	$\theta = 3.1–43.1°$
$c = 5.4505$ (6) Å	$\mu = 8.45$ mm^{-1}
$\alpha = 84.6178$ (17)°	$T = 100$ K
$\beta = 71.450$ (2)°	Irregular, black
$\gamma = 84.719$ (2)°	$0.06 \times 0.05 \times 0.04$ mm
$V = 278.61$ (3) Å^3	

Data collection

Bruker KAPPA APEX II CCD diffractometer	4889 independent reflections
	3222 reflections with $I > 3\sigma(I)$
Radiation source: X-ray tube	$R_{int} = 0$
$\omega–$ and $\varphi–$scans	$\theta_{max} = 43.3°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*TWINABS*; Bruker, 2016)	$h = -9 \rightarrow 13$
	$k = -15 \rightarrow 15$
$T_{min} = 0.60$, $T_{max} = 0.71$	$l = -10 \rightarrow 8$
4889 measured reflections	

Refinement

Refinement on F^2	31 constraints
$R[F > 3\sigma(F)] = 0.042$	Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0004I^2)$
$wR(F) = 0.102$	
$S = 1.18$	$(\Delta/\sigma)_{max} = 0.033$
4889 reflections	$\Delta\rho_{max} = 1.51$ e Å^{-3}
110 parameters	$\Delta\rho_{min} = -1.54$ e Å^{-3}
0 restraints	

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

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Mn1	0.15957 (12)	0.14823 (12)	0.81536 (13)	0.01408 (14)	0.798 (6)
Zn1	0.15957 (12)	0.14823 (12)	0.81536 (13)	0.01408 (14)	0.202 (6)
Mn2	0.65228 (11)	0.66509 (12)	0.81776 (13)	0.01226 (13)	0.814 (6)
Zn2	0.65228 (11)	0.66509 (12)	0.81776 (13)	0.01226 (13)	0.186 (6)
V1	0.82775 (17)	0.42761 (14)	0.2411 (4)	0.0085 (2)	0.843 (8)
V2	0.30349 (16)	0.90968 (14)	0.2939 (4)	0.0087 (2)	0.843 (8)
O1	0.2108 (3)	0.7627 (2)	0.5378 (4)	0.0460 (9)	
O2	0.4504 (3)	0.1638 (3)	0.8831 (5)	0.0211 (7)	
O3	0.9200 (3)	0.6445 (3)	0.9442 (5)	0.0194 (6)	
O4	0.3676 (5)	0.5738 (5)	0.8803 (8)	0.0201 (8)	
O5	0.8601 (5)	0.0706 (5)	0.8909 (7)	0.0159 (7)	
O6	0.6985 (5)	0.9047 (5)	0.5740 (7)	0.0146 (7)	
O7	0.2033 (6)	0.4225 (5)	0.5525 (7)	0.0231 (9)	
V2'	0.3230 (8)	0.9268 (7)	0.2381 (15)	0.0087 (2)	0.157 (8)
V1'	0.8062 (8)	0.4121 (7)	0.2971 (14)	0.0085 (2)	0.157 (8)

Atomic displacement parameters (Å^2) for (sc)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01089 (16)	0.0189 (2)	0.0134 (2)	−0.00258 (14)	−0.00335 (11)	−0.00575 (13)
Zn1	0.01089 (16)	0.0189 (2)	0.0134 (2)	−0.00258 (14)	−0.00335 (11)	−0.00575 (13)
Mn2	0.01074 (17)	0.0135 (2)	0.0134 (2)	−0.00149 (13)	−0.00385 (11)	−0.00406 (11)
Zn2	0.01074 (17)	0.0135 (2)	0.0134 (2)	−0.00149 (13)	−0.00385 (11)	−0.00406 (11)
V1	0.0062 (2)	0.0103 (2)	0.0080 (5)	−0.00016 (15)	−0.0004 (2)	−0.0025 (2)
V2	0.0093 (2)	0.0075 (2)	0.0100 (5)	0.00110 (15)	−0.0043 (2)	−0.0010 (2)
O1	0.0686 (14)	0.0310 (12)	0.0429 (13)	−0.0105 (10)	−0.0285 (11)	0.0218 (9)
O2	0.0153 (8)	0.0207 (9)	0.0328 (13)	0.0077 (6)	−0.0143 (6)	−0.0145 (7)
O3	0.0158 (8)	0.0173 (8)	0.0278 (12)	0.0080 (6)	−0.0114 (6)	−0.0087 (6)
O4	0.0159 (11)	0.0195 (12)	0.0279 (13)	−0.0015 (9)	−0.0110 (10)	−0.0010 (11)
O5	0.0135 (10)	0.0153 (10)	0.0210 (11)	−0.0010 (8)	−0.0085 (9)	−0.0002 (9)
O6	0.0189 (11)	0.0145 (10)	0.0122 (9)	−0.0016 (8)	−0.0060 (8)	−0.0048 (8)
O7	0.0254 (12)	0.0275 (15)	0.0198 (12)	0.0051 (10)	−0.0097 (10)	−0.0159 (12)
V2'	0.0093 (2)	0.0075 (2)	0.0100 (5)	0.00110 (15)	−0.0043 (2)	−0.0010 (2)
V1'	0.0062 (2)	0.0103 (2)	0.0080 (5)	−0.00016 (15)	−0.0004 (2)	−0.0025 (2)

Geometric parameters (Å, º) for (sc)

Mn1—O2	2.157 (3)	V1—V1'	0.313 (7)
Mn1—O3^i	2.119 (3)	V2—O1	1.683 (2)
Mn1—O5^{ii}	2.100 (4)	V2—O2^{iii}	1.734 (2)
Mn1—O6^{iii}	2.099 (3)	V2—O5^{iii}	1.719 (5)
Mn2—O2^i	2.121 (3)	V2—O6^v	1.693 (4)
Mn2—O3	2.145 (3)	V2—V2'	0.314 (7)
Mn2—O4	2.059 (4)	O1—V2'	1.983 (7)
Mn2—O6	2.198 (4)	O1—V1^{iiii}	1.570 (6)
Mn2—O7^{iii}	2.098 (4)	O2—V2^{iiii}	1.611 (5)
Zn2—O4	2.059 (4)	O3—V1^{iv}	1.960 (5)
V1—O1^{iii}	1.822 (2)	O4—V1^{iiii}	1.749 (9)

V1—O3^{iv}	1.776 (2)	O5—V2^{iiii}	1.621 (9)
V1—O4^{iii}	1.674 (5)	O6—V2^{iv}	1.724 (8)
V1—O7^{iii}	1.664 (5)	O7—V1^{iiii}	1.594 (8)
O2—Mn1—O3^{i}	80.79 (10)	Mn2^{i}—O2—V2^{iiii}	128.8 (3)
O2—Mn1—O5^{ii}	156.43 (13)	V2^{iii}—O2—V2^{iiii}	9.9 (3)
O2—Mn1—O6^{iii}	92.92 (13)	Mn1^{i}—O3—Mn2	98.25 (9)
O3^{i}—Mn1—O5^{ii}	97.32 (12)	Mn1^{i}—O3—V1^{iv}	126.60 (15)
O3^{i}—Mn1—O6^{iii}	140.58 (13)	Mn1^{i}—O3—V1^{riv}	125.7 (2)
O5^{ii}—Mn1—O6^{iii}	102.73 (16)	Mn2—O3—V1^{iv}	125.62 (17)
O2^{i}—Mn2—O3	81.01 (10)	Mn2—O3—V1^{riv}	120.7 (3)
O2^{i}—Mn2—O4	95.27 (13)	V1^{iv}—O3—V1^{riv}	7.8 (2)
O2^{i}—Mn2—O6	81.62 (12)	Mn2—O4—Zn2	0.0 (5)
O2^{i}—Mn2—O7^{iii}	159.11 (14)	Mn2—O4—V1^{iii}	144.3 (2)
O3—Mn2—O4	144.71 (14)	Mn2—O4—V1^{iiii}	134.3 (3)
O3—Mn2—O6	100.88 (13)	Zn2—O4—V1^{iii}	144.3 (2)
O3—Mn2—O7^{iii}	97.24 (14)	Zn2—O4—V1^{iiii}	134.3 (3)
O4—Mn2—O6	113.35 (16)	V1^{iii}—O4—V1^{iiii}	10.18 (19)
O4—Mn2—O7^{iii}	97.81 (17)	Mn1^{vi}—O5—V2^{iii}	131.7 (2)
O6—Mn2—O7^{iii}	78.26 (15)	Mn1^{vi}—O5—V2^{iiii}	141.9 (3)
O1^{iii}—V1—O3^{iv}	93.79 (11)	V2^{iii}—O5—V2^{iiii}	10.2 (2)
O1^{iii}—V1—O4^{iii}	101.47 (17)	Mn1^{iii}—O6—Mn2	109.52 (17)
O1^{iii}—V1—O7^{iii}	100.95 (18)	Mn1^{iii}—O6—V2^{v}	126.5 (2)
O1^{iii}—V1—V1'	33.3 (10)	Mn1^{iii}—O6—V2^{rv}	136.8 (3)
O3^{iv}—V1—O4^{iii}	119.67 (19)	Mn2—O6—V2^{v}	120.5 (2)
O3^{iv}—V1—O7^{iii}	119.76 (18)	Mn2—O6—V2^{rv}	110.3 (3)
O3^{iv}—V1—V1'	122.0 (10)	V2^{v}—O6—V2^{rv}	10.5 (2)
O4^{iii}—V1—O7^{iii}	113.9 (2)	Mn2^{iii}—O7—V1^{iii}	148.9 (2)
O4^{iii}—V1—V1'	98.8 (12)	Mn2^{iii}—O7—V1^{iiii}	138.5 (3)
O7^{iii}—V1—V1'	71.8 (12)	V1^{iii}—O7—V1^{iiii}	10.7 (2)
O1—V2—O2^{iii}	107.63 (12)	V2—V2'—O1	15.6 (10)
O1—V2—O5^{iii}	106.84 (16)	V2—V2'—O2^{iii}	108.0 (11)
O1—V2—O6^{v}	107.87 (17)	V2—V2'—O5^{iii}	103.0 (12)
O1—V2—V2'	161.6 (12)	V2—V2'—O6^{v}	79.0 (13)
O2^{iii}—V2—O5^{iii}	111.34 (18)	O1—V2'—O2^{iii}	99.7 (3)
O2^{iii}—V2—O6^{v}	112.52 (16)	O1—V2'—O5^{iii}	98.1 (3)
O2^{iii}—V2—V2'	62.1 (10)	O1—V2'—O6^{v}	94.5 (4)
O5^{iii}—V2—O6^{v}	110.4 (2)	O2^{iii}—V2'—O5^{iii}	123.8 (5)
O5^{iii}—V2—V2'	66.7 (13)	O2^{iii}—V2'—O6^{v}	117.3 (4)
O6^{v}—V2—V2'	90.5 (12)	O5^{iii}—V2'—O6^{v}	113.7 (3)
V1^{iii}—O1—V2	165.08 (13)	V1—V1'—O1^{iii}	140.5 (12)
V1^{iii}—O1—V2'	163.00 (19)	V1—V1'—O3^{iv}	50.2 (8)
V1^{iii}—O1—V1^{iiii}	6.3 (2)	V1—V1'—O4^{iii}	71.1 (13)
V2—O1—V2'	2.9 (2)	V1—V1'—O7^{iii}	97.5 (12)
V2—O1—V1^{iiii}	159.2 (2)	O1^{iii}—V1'—O3^{iv}	95.6 (3)
V2'—O1—V1^{iiii}	156.9 (3)	O1^{iii}—V1'—O4^{iii}	109.2 (4)
Mn1—O2—Mn2^{i}	97.82 (8)	O1^{iii}—V1'—O7^{iii}	116.5 (5)
Mn1—O2—V2^{iii}	130.06 (17)	O3^{iv}—V1'—O4^{iii}	107.0 (4)
Mn1—O2—V2^{iiii}	133.3 (3)	O3^{iv}—V1'—O7^{iii}	113.3 (3)
Mn2^{i}—O2—V2^{iii}	131.17 (16)	O4^{iii}—V1'—O7^{iii}	113.5 (4)

Symmetry codes: (i) −x+1, −y+1, −z+2; (ii) x−1, y, z; (iii) −x+1, −y+1, −z+1; (iv) −x+2, −y+1, −z+1; (v) −x+1, −y+2, −z+1; (vi) x+1, y, z.

Comparison of atomic positions in the M phase (derived from the powder synchrotron refinement), represented in a pseudo-monoclinic unit cell, M′, defined by Zhuravlev et al. (1993), and their corresponding positions in β-Mn₂V₂O₇ representing the more general β-(Mn,Zn)₂V₂O₇ high temperature solid solution.

Atom (M′)	Atom (β)	x(M′)	y(M′)	z(M′)	x(β)	y(β)	z(β)	Δx	Δy	Δz	Shift (Å)
(Mn/Zn)1	Mn	0.0044	0.8102	−0.0145	0.0	0.8109	0.0	−0.0044	0.0007	0.0145	0.084
(Mn/Zn)2	Mn	0.0011	0.8177	0.0117	0.0	0.8109	0.0	−0.0011	−0.0068	−0.0117	0.082
V1	V	0.7551	0.0011	0.3982	0.7341	0.0	0.4032	−0.0210	−0.0011	0.0050	0.149
V2	V	0.7126	−0.0023	0.3962	0.7341	0.0	0.4032	0.0215	0.0023	0.0070	0.142
O1	O1	0.5386	0.0055	0.5542	0.5	0.0	0.5	−0.0386	−0.0055	−0.0542	0.330
O2	O2	0.8826	−0.0029	0.7031	0.9093	0.0	0.7191	0.0267	0.0029	0.0160	0.180
O3	O2	0.9447	0.0049	0.7227	0.9093	0.0	0.7191	−0.0354	−0.0049	−0.0036	0.238
O4	O3	0.7231	0.1593	0.2019	0.7322	0.1614	0.2123	0.0091	0.0021	0.0104	0.072
O5	O3	0.7271	0.1585	0.2121	0.7322	0.1614	0.2123	0.0051	0.0029	0.0002	0.043
O6	O3	0.7366	0.1598	0.2107	0.7322	0.1614	0.2123	−0.0044	0.0016	0.0016	0.036
O7	O3	0.7073	0.1590	0.2226	0.7322	0.1614	0.2123	0.0249	0.0024	−0.0103	0.187

Note: The components Δx, Δy and Δz of the shifts and the magnitudes of the shifts are all defined with respect to the β-Mn₂V₂O₇ set of basis vectors quoted by Liao *et al.* (1996).

Selected bond lengths and angles (Å, °)

	Powder data	Single crystal data
(Mn/Zn)1—O5[i]	2.107 (2)	2.100 (4)
(Mn/Zn)1—O6[ii]	2.111 (2)	2.099 (3)
(Mn/Zn)1—O3[iii]	2.143 (2)	2.119 (3)
(Mn/Zn)1—O2	2.187 (2)	2.157 (3)
(Mn/Zn)1—O5[iv]	2.242 (2)	2.229 (4)
(Mn/Zn)1—O7	2.538 (2)	2.474 (4)
(Mn/Zn)2—O4	2.082 (2)	2.059 (4)
(Mn/Zn)2—O7[ii]	2.097 (2)	2.098 (4)
(Mn/Zn)2—O3	2.156 (2)	2.145 (3)
(Mn/Zn)2—O2[iii]	2.165 (2)	2.121 (3)
(Mn/Zn)2—O6	2.216 (2)	2.198 (4)
(Mn/Zn)2—O4[iii]	2.328 (2)	2.371 (4)
V1—O7[ii]	1.636 (2)	1.664 (5)
V1—O4[ii]	1.679 (3)	1.674 (5)
V1—O1[ii]	1.785 (2)	1.822 (2)
V1—O3[v]	1.801 (2)	1.776 (2)
V1—O3[vi]	2.209 (2)	2.234 (3)
V1′—O7[ii]	-	1.594 (8)
V1′—O4[ii]	-	1.749 (9)
V1′—O1[ii]	-	1.570 (6)
V1′—O3[v]	-	1.960 (5)
V2—O2[ii]	1.674 (2)	1.734 (2)
V2—O6[vii]	1.684 (2)	1.693 (4)
V2—O5[ii]	1.692 (3)	1.719 (5)
V2—O1	1.737 (2)	1.683 (2)

V2'—O2^{ii}	-	1.611 (5)
V2'—O6^{vii}	-	1.724 (8)
V2'—O5^{ii}	-	1.621 (9)
V2'—O1	-	1.983 (7)
V2—O1—V1^{ii}	162.74 (11)	165.08 (13)
V2—O1—V1^{vii}	-	159.2 (2)
V2'—O1—V1^{vii}	-	156.9 (3)
V2'—O1—V1^{ii}	-	163.00 (19)

Symmetry codes: (i) x-1, y, z; (ii) -x+1, -y+1, -z+1; (iii) -x+1, -y+1, -z+2; (iv) -x+1, -y, -z+2; (v) -x+2, -y+1, -z+1; (vi) x, y, z-1; (vii) -x+1, -y+2, -z+1.