# X-ray powder diffraction and electron diffraction studies of the thortveitite-related $L$ phase, $(Zn,Mn)_2V_2O_7$

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# SUPPLEMENTARY DATA

# 1.      Transmission electron microscopy

## 1.1      The [ 1 $\bar{1}$ 0 ] electron diffraction pattern

An example of a low index zone electron diffraction pattern of particular interest from $L$ phase in the context of the structure proposed by Zhuravlev $et$ $al.$ (1993) is shown in Fig. 1. This particular electron diffraction pattern can also be obtained from the phase designated $\gamma$-$Zn_3(VO_4)_2$ elsewhere in the literature, but is not one of those in the published papers. In this [ 1$\bar{1}$0 ] zone, the reciprocal lattice vectors labelled 001 and 110 correspond to interplanar spacings of 9.33 Å and 6.59 Å respectively using the unit cell parameters proposed by Hng & Knowles (1999). These are the two shortest reciprocal lattice vector types predicted for the monoclinic C unit cell, with a length ratio of 1:1.416. This ratio compares well with the measured ratio of 1:1.405 from this electron diffraction pattern. The measured angle between these two reciprocal lattice vectors is 84.5°, in reasonable agreement with a calculated angle of 84.37°. By comparison, candidate $hkl$ indices for these reciprocal lattice vectors using the unit cell parameters of $a$ = 13.342 Å, $b$ = 8.559 Å, $c$ = 9.976 Å and $\beta$ = 105.81° proposed by Zhuravlev $et$ $al.$ (1993) for the $L$ phase at a composition $(Zn_{0.7}Mn_{0.3})_2V_2O_7$, fail to account for Fig. 1 (Table 1), even allowing for reasonable uncertainties in the camera length in the transmission electron microscope and the ratio of the interplanar spacings of the two reciprocal lattice vectors. It can therefore be concluded from the analysis of this electron diffraction pattern that the unit cell proposed by Zhuravlev $et$ $al.$ (1993) for the $L$ phase is incorrect.

## 1.2    The [102] convergent beam electron diffraction pattern

A particularly convincing demonstration from convergent beam electron diffraction that the space group of the $L$ phase is $Cm$ rather than $C2/m$ is shown in Fig. 2. The zone axis symmetry is $m$. If the zone axis symmetry were $2_\mathrm{R}mm_\mathrm{R}$, the point group would be $2/m$. In this context, the subscript R refers to an operator which rotates each dark-field image through 180° about its own centre (Buxton *et al.*, 1976). Inspection of Fig. 2 shows that the features seen in the dark field images are inconsistent with $2_\mathrm{R}mm_\mathrm{R}$.

## 2.    Transformed atomic positions of β'-Zn₂V₂O₇

An atom at a vector position $[uvw]_{\beta'}$ relative to the origin becomes an atom at $[UVW]_L$, where

$$
\begin{bmatrix} U \\ V \\ W \end{bmatrix}_L = \begin{bmatrix} -\dfrac{1}{3} & 0 & -\dfrac{1}{3} \\ 0 & -1 & 0 \\ \dfrac{2}{3} & 0 & \dfrac{1}{3} \end{bmatrix} \begin{bmatrix} u \\ v \\ w \end{bmatrix}_{\beta'}
$$

The resultant atomic positions for this initial model are shown in Table 2. The final atomic positions for the $L$ phase in Table 3 of the paper are very similar to these starting atomic positions for the Rietveld refinement.

# References

Buxton, B. F., Eades, J. A., Steeds, J. W. & Rackham, G. M. (1976). *Phil. Trans. Roy. Soc. A* **281**, 171–194.

Hng, H.-H. & Knowles, K. M. (1999). *J. Eur. Ceram. Soc.* **19**, 721–726.

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 Captions

Fig. 1  $[1\bar{1}0]$ zone selected area diffraction pattern from the *L* phase showing the 001 and 110 reciprocal lattice vectors which together subtend an acute angle of 84.5° at the origin, 000.

Fig. 2  Convergent beam electron diffraction pattern from the [102] zone of the *L* phase, courtesy of H.H. Hng.

Table 1: Selected calculated interplanar spacings, $d_{hkl}$, and angles between reciprocal lattice vectors from the unit cell for $L$ phase with a composition $(Zn_{0.7}Mn_{0.3})_2V_2O_7$ proposed by Zhuravlev *et al.* (1993).

| $h_1k_1l_1$ | $d_{h_1k_1l_1}$ (Å) | $h_2k_2l_2$ | $d_{h_2k_2l_2}$ (Å) | $d_{h_1k_1l_1}/d_{h_2k_2l_2}$ | Angle (°) |
|---|---|---|---|---|---|
| 001 | 9.59861 | 101 | 6.84481 | 1.402 | 30.87 |
| 001 | 9.59861 | 200 | 6.41864 | 1.495 | 74.19 |
| 001 | 9.59861 | 011 | 6.38818 | 1.503 | 48.28 |
| 001 | 9.59861 | $01\bar{1}$ | 6.38818 | 1.503 | 48.28 |
| | | | | | |
| $10\bar{1}$ | 8.94434 | $\bar{1}0\bar{1}$ | 6.84481 | 1.307 | 72.96 |
| $10\bar{1}$ | 8.94434 | 200 | 6.41864 | 1.393 | 63.71 |
| $10\bar{1}$ | 8.94434 | $0\bar{1}\bar{1}$ | 6.38818 | 1.400 | 60.41 |
| $10\bar{1}$ | 8.94434 | $11\bar{1}$ | 6.18387 | 1.446 | 46.26 |
| $10\bar{1}$ | 8.94434 | $20\bar{1}$ | 6.16837 | 1.450 | 25.52 |

Table 2:       Atomic positions for the initial crystal structure model for $L$ phase based on the crystal structure of β'-$Zn_2V_2O_7$. Space group C2/$m$.

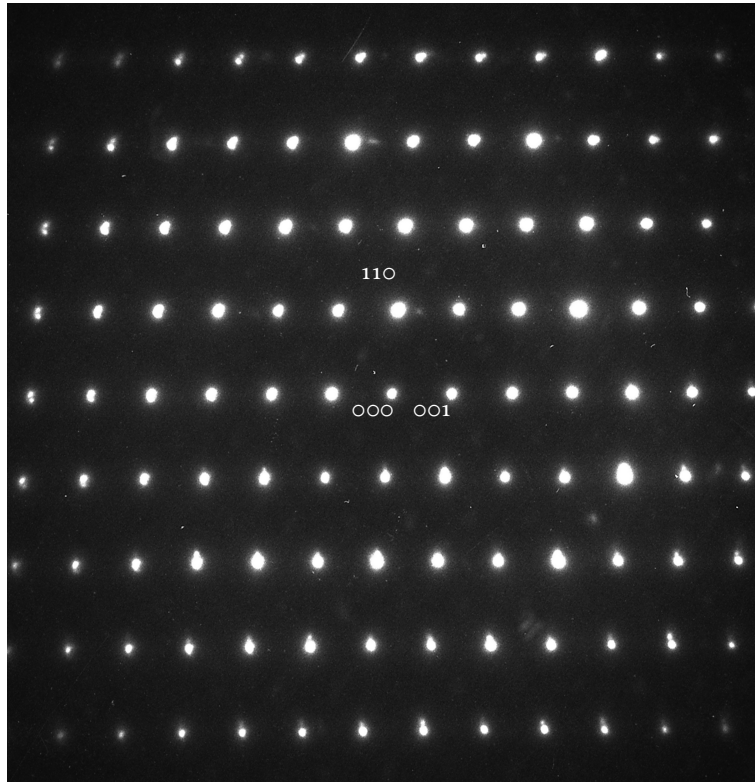| Atom | Position | $x/a$ | $y/b$ | $z/c$ |
|------|----------|-------|-------|-------|
| Zn(1) | 8$j$ | 0.33333 | 0.81577 | 0.16667 |
| Zn(2) | 4$h$ | 0 | 0.81577 | 0.5 |
| V(1) | 4$i$ | 0.04075 | 0 | 0.17661 |
| V(2) | 4$i$ | 0.37409 | 0 | 0.84327 |
| V(3) | 4$i$ | 0.70742 | 0 | 0.50994 |
| O(1a) | 4$i$ | 0.33333 | 0 | 0.66667 |
| O(1b) | 2$a$ | 0 | 0 | 0 |
| O(2a) | 8$j$ | 0.02547 | 0.1519 | 0.75943 |
| O(2b) | 8$j$ | 0.30787 | 0.1519 | 0.90723 |
| O(2c) | 8$j$ | 0.3588 | 0.1519 | 0.4261 |
| O(3a) | 4$i$ | 0.12863 | 0 | 0.46227 |
| O(3b) | 4$i$ | 0.46197 | 0 | 0.12893 |
| O(3c) | 4$i$ | 0.2047 | 0 | 0.2044 |

**Figure 1**

[ 1 $\bar{1}$ 0 ] zone selected area diffraction pattern fromthe $L$ phase showing the 001 and 110 reciprocal lattice vectors which together subtend an acute angle of 84.5° at the origin, 000.
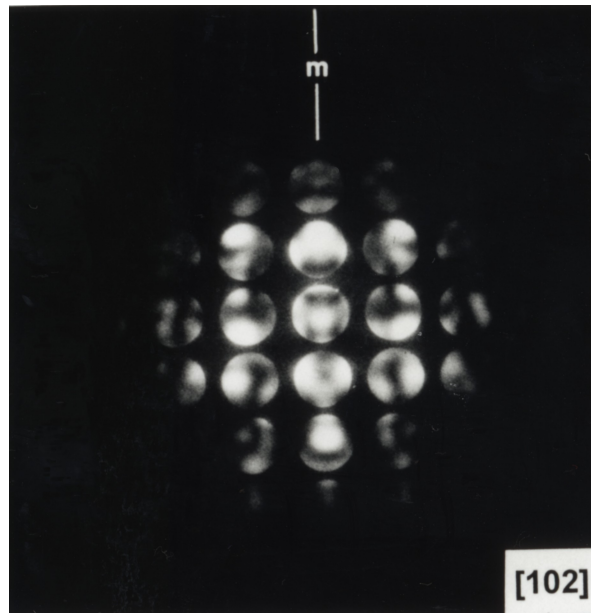
**Figure 2**

Convergent beam electron diffraction pattern from the [102] zone of the *L* phase, courtesy of H.H. Hng.