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# Cation ordering in the double tungstate $LiFe(WO_4)_2$

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Single crystals of lithium iron tungstate, $LiFe(WO_4)_2$, were obtained using a high-temperature solution growth method. The analysis was conducted using the monoclinic space group $C2/c$, with $\beta = 90.597$ (2)°, giving $R1 = 0.0177$. The Li and Fe atoms lie on twofold axes. The structure can also be refined using the orthorhombic space group *Cmcm*, giving slightly higher residuals. The experimental value of $\beta$ and the residuals mitigate in favour of the monoclinic description of the structure. Calculated bond-valence sums for the present results are closer to expected values than those obtained using the results of a previously reported analysis of this structure.

## Comment

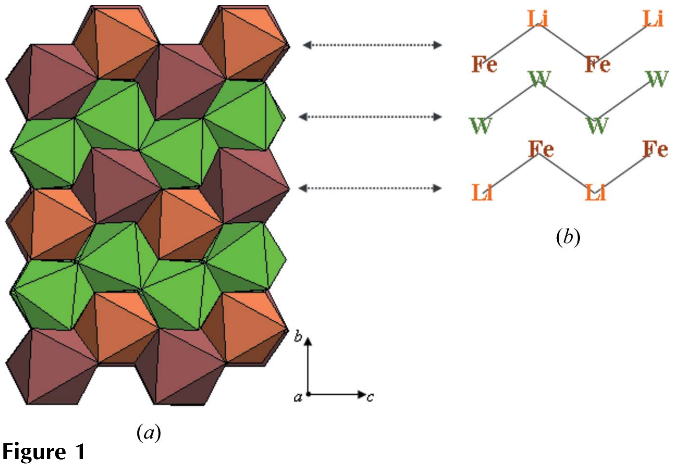
Cation distributions in the $A^{+}B^{3+}(WO_4)_2$ compounds of the wolframite structure [(Fe,Mn)$WO_4$] have been studied by Le Flem *et al.* (1969, 1970) and Salmon *et al.* (1970). The analyses performed on this family of compounds, known as 'double tungstates', showed that the distribution of cations in the wolframite structure depends on their relative sizes. Indeed, both homogeneous chains, encompassing a unique cation, and chains with alternating cations are encountered. Among these materials, $LiFe(WO_4)_2$ was previously obtained as single crystals and its structure was refined to $R = 0.149$ in the space group $C2/c$, with cell parameters similar to those presented in this study (Klevtsova & Belov, 1970; Klevtsov & Klevtsova, 1970; Klevtsov *et al.*, 1971).

When the previously reported structure of $LiFe(WO_4)_2$ was analysed using the bond-valence model (Brese & O'Keeffe, 1991), some inconsistencies arose regarding the iron–tungsten network. Though values of the oxygen and lithium valences were in good agreement with the expected values, the average cationic bond-valence sums (BVS) calculated for Fe and W were considerably different from what is expected, *viz.* $\nu_{Fe} = 3.90$ and $\nu_{W} = 5.32$ (Table 1). A possible explanation of these results could involve partial disorder of the iron and tungsten cations over their six-coordinate sites in the octahedral framework. Such a statistical Fe/W distribution between two distinct *B* sites is actually observed in perovskites with composition $A_3Fe_2WO_9$, with $A$ = Sr (Viola *et al.*, 2003), Ca (Ivanov *et al.*, 2005) and Ba (Ivanov *et al.*, 2006). But the structural model presented by Klevtsov *et al.* (1971) does not indicate any disorder. So, one could speculate that the refined structure was idealized while the real sample was not perfectly ordered. We report here the study of $LiFe(WO_4)_2$ crystals obtained by the flux method and displaying fully ordered cationic sublattices.

It is worth mentioning that our description of the $LiFe(WO_4)_2$ crystal structure could appear, at a first glance, compatible with higher symmetry, namely with the orthorhombic space group *Cmcm* (No. 63). However, the value of the cell angle $\beta$ [90.597 (2)°] cannot be assigned as 90° within experimental error. Furthermore, the refinement using *Cmcm* yields poorer values of the reliability factors: $R1 = 0.0362$ and $wR2 = 0.1488$ for *Cmcm* compared to $R1 = 0.0177$ and $wR2 = 0.0413$ for $C2/c$. The orthorhombic model requires disorder of the O atoms, which is neither required nor observed in the $C2/c$ model. Further, refinement with *Cmcm* gives unreasonable displacement parameters and is not, in any event, compatible with the observed $LiFe(WO_4)_2$ unit-cell $\beta$ angle. The Li, Fe and W atoms, as refined with the space group $C2/c$, do adhere quite well to *Cmcm* symmetry, and the O atoms are the only ones that clearly require the lower-symmetry description.

According to the bond-valence analysis of the results of our refinement (Tables 2 and 3), the structure of $LiFe(WO_4)_2$ displays full order as far as the Fe and W ions are concerned. This time the values of the BVS calculation for all ions were in very good agreement with the theoretical ones.

$LiFe(WO_4)_2$ is based on a distorted hexagonal packing of O atoms and is closely related to the wolframite structure. The structure is built of two kinds of chains of edge-sharing octahedra, which are propagated along [010] (Fig. 1). The first type of chain contains $Li^{+}$ and $Fe^{3+}$ ions (both on twofold axes, Wyckoff sites 4*e*, formula $[Li_{0.5}Fe_{0.5}O_4]^{6-}$). The second chain is composed of tungstate units on general positions (formula $[WO_4]^{2-}$). The overall structure is the union of these two types of chains by corner sharing. All cations have octahedral



(*b*)

(*a*)

**Figure 1**
(*a*) The octahedral layers of Li, Fe and W in the crystal structure of $LiFe(WO_4)_2$, viewed along [100], and (*b*) a representation of the alternating zigzag cation chains.

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coordination with bond lengths (Table 3) very close to the values expected on the basis of ionic radii (Shannon, 1976).

No structural data have been reported for $LiFe(WO_4)_2$ since 1970, although a recent work on positive electrode materials for rechargeable lithium batteries (Li & Fu, 2008) reported the electrochemical characterization of $LiFe(WO_4)_2$. Our present structural study of this double tungstate provides a more accurate escription of its crystal structure than has been available up to now.

## Experimental

Monoclinic crystals of $LiFe(WO_4)_2$ were obtained using a classical high-temperature solution growth procedure (Elwell & Scheel, 1975), in an attempt to grow an iron tungstate using $LiBO_2$ as solvent. During this experiment, the flux reacted with the iron tungstate to form $LiFe(WO_4)_2$.

### *Crystal data*

$LiFe(WO_4)_2$
$M_r = 558.46$
Monoclinic, $C2/c$
$a = 9.2884\ (3)$ Å
$b = 11.4181\ (3)$ Å
$c = 4.9018\ (1)$ Å
$\beta = 90.597\ (2)^\circ$
$V = 519.84\ (2)$ Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 46.90$ mm$^{-1}$
$T = 293$ K
0.15 × 0.03 × 0.02 mm

### *Data collection*

Nonius KappaCCD diffractometer
Absorption correction: Gaussian; grid of 8 × 8 × 52 = 3328 sampling points
$T_{\min} = 0.090$, $T_{\max} = 0.630$
11306 measured reflections
906 independent reflections
827 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.081$

### *Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.041$
$S = 1.12$
906 reflections
57 parameters
$\Delta\rho_{\max} = 1.67$ e Å$^{-3}$
$\Delta\rho_{\min} = -2.57$ e Å$^{-3}$

**Table 1**
Bond-valence analysis using interatomic distances reported by Klevtsov & Klevtsova (1970).

| Atom | Li1 | Fe1 | W1 | V(O) |
|---|---|---|---|---|
| O1 |  | 2 × 0.83 | 0.74 | 1.88 |
|  |  |  | 0.31 |  |
| O2 | 2 × 0.16 | 2 × 0.68 | 1.15 | 1.99 |
| O3 | 2 × 0.18 |  | 1.03 | 1.88 |
|  |  |  | 0.67 |  |
| O4 | 2 × 0.18 | 2 × 0.44 | 1.42 | 2.04 |
| V(cation) | 1.03 | 3.90 | 5.32 |  |

**Table 2**
Bond-valence parameters derived from the present refinement.

| Atom | Li1 | Fe1 | W1 | V(O) |
|---|---|---|---|---|
| O1 |  | 2 × 0.584 | 0.915 ($O1^{iv}$) | 1.966 |
|  |  |  | 0.467 ($O1^{v}$) |  |
| O2 | 2 × 0.108 | 2 × 0.524 | 1.391 | 2.023 |
| O3 | 2 × 0.193 |  | 1.179 | 2.026 |
|  |  |  | 0.654 ($O3^{v}$) |  |
| O4 | 2 × 0.169 | 2 × 0.408 | 1.468 | 2.045 |
| V(cation) | 0.94 | 3.032 | 6.073 |  |

Symmetry codes: (iv) $x, y, z - 1$; (v) $x, -y, z - \frac{1}{2}$.

**Table 3**
Interatomic distances (Å) from the present analysis of $LiFe(WO_4)_2$.

The shortest $M\cdots M$ and $O\cdots O$ distances are also listed. The $d_{\rm calc}$ values are the sums of ionic radii as given by Shannon (1976).

| Atoms *i,j* | $d_{ij}$ | Atoms *i,j* | $d_{ij}$ |
|---|---|---|---|
| $Li1-O3^{i},O3^{iii}$ | 2.075 (6) | $Fe1-O1,O1^{viii}$ | 1.958 (3) |
| $Li1-O4^{ii},O4^{vi}$ | 2.124 (3) | $Fe1-O2,O2^{viii}$ | 1.998 (3) |
| $Li1-O2,O2^{vii}$ | 2.288 (7) | $Fe1-O4^{iii},O4^{vi}$ | 2.091 (3) |
| $\langle Li-O\rangle$ | 2.163 (5) | $\langle Fe-O\rangle$ | 2.016 (3) |
| $d_{\rm calc}(Li^{+}-O^{2-})$ | 2.14 | $d_{\rm calc}(Fe^{3+}-O^{2-})$ | 2.045 |
|  |  |  |  |
| $W1-O4$ | 1.779 (3) |  |  |
| $W1-O2$ | 1.799 (3) | $Fe1\cdots Li1$ | 3.181 (5) |
| $W1-O3$ | 1.860 (3) | $W1\cdots W1^{v}$ | 3.219 (1) |
| $W1-O1^{iv}$ | 1.954 (3) | $Li1\cdots W1^{ii}$ | 3.405 (9) |
| $W1-O3^{v}$ | 2.078 (3) | $O1\cdots O3^{ix}$ | 2.460 (4) |
| $W1-O1^{v}$ | 2.203 (3) |  |  |
| $\langle W-O\rangle$ | 1.946 (3) |  |  |
| $d_{\rm calc}(W^{6+}-O^{2-})$ | 1.98 |  |  |

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iv) $x, y, z - 1$; (v) $x, -y, z - \frac{1}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $1 - x, y, -z + \frac{1}{2}$; (viii) $1 - x, y, -z + \frac{3}{2}$; (ix) $x, -y, z + \frac{1}{2}$.

Data collection: *COLLECT* (Bruker, 2008); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3264). Services for accessing these data are described at the back of the journal.

## References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Bruker (2008). *COLLECT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Elwell, D. & Scheel, H. J. (1975). In *Crystal Growth from High-temperature Solutions*. London: Academic Press.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Ivanov, S. A., Eriksson, S. G., Tellgren, R. & Rundlof, H. (2005). *J. Solid State Chem.* **178**, 3605–3614.

Ivanov, S. A., Eriksson, S. G., Tellgren, R., Rundlof, H., Nordblad, P. & Eriksen, J. (2006). *J. Solid State Chem.* **179**, 2645–2655.

Klevtsova, R. F. & Belov, N. V. (1970). *Sov. Phys. Crystallogr.* **15**, 32–35.

Klevtsov, P. V., Demenev, A. V. & Klevtsova, R. F. (1971). *Sov. Phys. Crystallogr.* **16**, 440–445.

Klevtsov, P. V. & Klevtsova, R. F. (1970). *Sov. Phys. Crystallogr.* **15**, 245–248.

Le Flem, G., Salmon, R. & Hagenmuller, P. (1969). *C. R. Acad. Sci. Paris*, **268**, 1431–1434.

Le Flem, G., Salmon, R. & Hagenmuller, P. (1970). *C. R. Acad. Sci. Paris*, **270**, 543–546.

Li, C.-L. & Fu, Z.-W. (2008). *Electrochim. Acta*, **53**, 6434–6443.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Salmon, R., Casalot, A., Le Flem, G. & Hagenmuller, P. (1970). *Mater. Res. Bull.* **5**, 341–352.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Viola, M. del C., Augsburger, M. S., Pinacca, R. M., Pedregosa, J. C., Carbonio, R. E. & Mercaderc, R. C. (2003). *J. Solid State Chem.* **175**, 252–257.