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# $Ca_2MgWO_6$ from neutron and X-ray powder data

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The room-temperature structure of the *B*-site-ordered complex perovskite dicalcium magnesium tungstate, $Ca_2MgWO_6$, has been determined by simultaneous Rietveld refinement of neutron and X-ray powder diffraction patterns. $Ca_2MgWO_6$ is characterized by *B*-site ordering and an $a^-a^-c^+$-type $BO_6$ octahedral tilt mechanism.

## Comment

Various perovskite compounds whose *B* sites are occupied by two cation species have been synthesized to date, and their crystal structures have been determined (Galasso, 1969). These compounds have the general chemical formula $AB_xB_{1-x}O_3$. When the differences in ionic radii or charges between two different *B*-site cations increase, ordering of the *B*-site cations may occur, giving rise to different crystal structures (Setter & Cross, 1980). The ideal structure of the *B*-site-ordered complex perovskite $A_2B'B''O_6$ is a centered space group ($Fm3m$) resulting from the alternation of *B*-site cations.

The real perovskite structure often deviates from the ideal cubic structure, and $BO_6$ octahedral tilting is the most common distortion mechanism. This type of distortion is typically observed when the tolerance factor (Goldschmidt, 1926) is smaller than 1, which means that the *A*-site cation is small compared with the cubic $BO_6$ corner-sharing octahedral network.

Octahedral tilting in perovskites was first examined by Megaw & Darlington (1975), and fundamental work was carried out by Glazer (1972, 1975). The latter work demonstrated that the space group is determined largely by the pattern of in-phase ($a^+$), antiphase ($a^-$) and null ($a^0$) octahedral tilting along one of the Cartesian coordinate axes. A classification of octahedral tilting in terms of 23 alternative tilt systems was also proposed. Woodward (1997*a*) predicted the space groups that arise from the combination of octahedral tilting and *B*-site cation ordering. When the two $B-O$ bond distances are non-equivalent, the rigid rotation of octahedra in the connected $B'O_6$ and $B''O_6$ network can be inhibited for certain tilt systems.

Although, the crystal structures of simple prototype perovskites have been investigated thoroughly, only a few structural studies of *B*-site-ordered complex perovskites have been performed. In this paper, we present a detailed structure determination of the title compound, $Ca_2MgWO_6$, (I).

Compound (I) is an example of a *B*-site-ordered complex perovskite-type material. The $Mg^{2+}$ and $W^{6+}$ cations are located at alternate *B* sites as a result of the large difference between the valence charges of these cations. The simultaneous Rietveld refinement of the neutron and X-ray data (Fig. 1) measured for (I) shows that the present structure (Fig. 2) is monoclinic, in space group $P2_1/n$, and is characterized by *B*-site cation ordering and $a^-a^-c^+$-type $BO_6$ octahedral tilting. The antiparallel shift of the *A*-site cation, approximately along the [010] monoclinic direction, often accompanies octahedral tilting, as observed for the $CaTiO_3$ system (Kay & Bailey, 1957). The present structure is isomorphous with $Sr_2YbNbO_6$ (Yang *et al.*, 1999), in which the *B*-site cations are ordered because of the large difference in their ionic sizes.

The average Mg—O and W—O distances for the $BO_6$ octahedra are 2.069 and 1.922 Å, respectively. These values are in good agreement with those predicted by the ionic radii

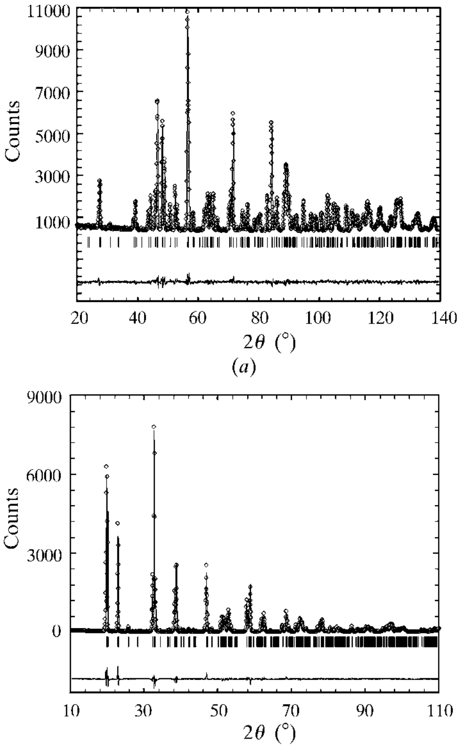

**Figure 1**
A comparison of the observed (circles) and calculated (solid line) intensities for (I), obtained from (*a*) neutron diffraction and (*b*) X-ray diffraction data. The difference pattern appears below.

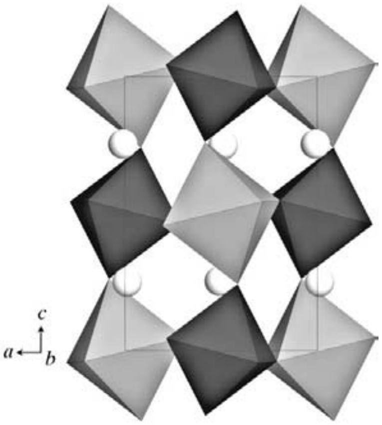

**Figure 2**
The structure of (I) projected on to the (010) plane. The $BO_6$ octahedral tilt about the *b* axis is shown. $MgO_6$ and $WO_6$ groups are shown as light-gray and dark-gray polyhedra, respectively, and Ca atoms are shown as white circles.

of Shannon (1976) [$r(\mathrm{Mg}^{2+}) = 0.86$ Å, $r(\mathrm{W}^{6+}) = 0.74$ Å and $r(\mathrm{O}^{2-}) = 1.28$ Å]. However, both types of octahedra are slightly distorted from the ideal cubic case, in order to maintain the corner-sharing network (Table 1).

Thomas (1989, 1996) and Woodward (1997*b*) found that the *A* cation strongly favors the crystallographically equivalent site, thus maximizing the *A*-cation polyhedral volume when the octahedral tilt occurs. These authors also found that the orthorhombic $a^-a^-c^+$ tilt system provides the maximum number of short *A*—O bonds (four) when the tilt angle increases. The tolerance factor of (I) is 0.94, which is much smaller than 1, and the arrangement of the oxide ions around the $Ca^{2+}$ cation (Fig. 3) shows that four of the 12 Ca—O bonds are significantly shortened. The average length of these four short Ca—O bonds is 2.377 Å, which is close to the calculated value, assuming $Ca^{2+}$ ionic radii in sixfold coordination (1.00 Å). These findings agree with the predicted structure.

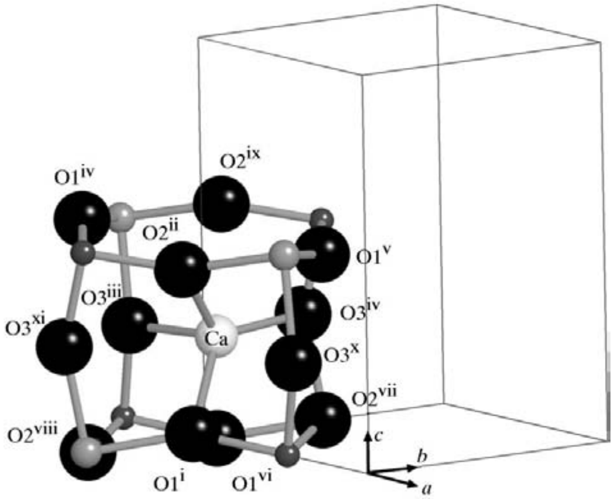

**Figure 3**
The coordination of oxide ions around a $Ca^{2+}$ cation in (I). Four short Ca—O bonds are shown (see Table 1 for symmetry codes).

## Experimental

The single-phase powder sample of $Ca_2MgWO_6$ was synthesized by a conventional solid-state reaction, using $CaCO_3$, MgO and $WO_3$ as starting materials. To avoid sublimation of $WO_3$, the precursor powder of $MgWO_4$ was prepared by calcination of a wet milled mixture of MgO and $WO_3$ in stoichiometric proportions at 1073 K for 10 h in air. The precursor was ground and mixed with a stoichiometric quantity of $CaCO_3$, and this mixture was milled and heated in air at 1573 K for 10 h.

*Crystal data*

$Ca_2MgWO_6$
$M_r = 384.3$
Monoclinic, $P2_1/n$
$a = 5.4199$ (1) Å
$b = 5.5479$ (1) Å
$c = 7.7147$ (2) Å
$\beta = 90.092$ (2)°
$V = 231.972$ (8) Å$^3$
$Z = 2$
$D_x = 5.5$ Mg m$^{-3}$
Irregular, white

## X-ray diffraction

*Crystal data*

Cu *Kα* radiation
$T = 293$ K
Specimen shape: flat sheet
25 × 25 × 1 mm

*Data collection*

Rigaku Rotaflex diffractometer
Specimen mounting: packed-powder sheet
Specimen mounted in reflection mode
$2\theta_{\min} = 10.3$, $2\theta_{\max} = 129.95$°
Increment in $2\theta = 0.05$°

*Refinement*

$R_p = 0.0702$
$R_{wp} = 0.1050$
$R_{exp} = 0.0844$
$S = 1.55$
Profile function: pseudo-Voigt
36 parameters
$(\Delta/\sigma)_{\max} = 0.01$

## Neutron diffraction

*Crystal data*

Neutron radiation
$\lambda = 1.8339$ Å
$\mu = 0.11$ mm$^{-1}$
$T = 293$ K
Specimen shape: cylinder
50 × 10 × 10 mm

*Data collection*

HANARO high-resolution powder diffractometer
Specimen mounting: packed-powder cylinder
Specimen mounted in transmission mode
$2\theta_{\min} = 0$°, $2\theta_{\max} = 159.95$°
Increment in $2\theta = 0.05$°

*Refinement*

$R_p = 0.0379$
$R_{wp} = 0.0495$
$R_{exp} = 0.0346$
$S = 2.04$
Profile function: pseudo-Voigt
36 parameters
$(\Delta/\sigma)_{\max} = 0.01$

The X-ray powder diffraction pattern was collected at room temperature using Cu *Kα* radiation. The neutron powder diffraction pattern was collected at room temperature with a high-resolution powder diffractometer at the HANARO reactor, Korea Atomic Energy Research Institute (KAERI). Neutrons from the ST2 channel of the reactor were monochromated by a vertically focusing composite Ge monochromator at a 90° take-off position. Cell parameters were obtained from the *WinPLOTR* program (Roisnel & Rodríguez-Carvajal, 2001) using the neutron diffraction profile, and analysis of the systematic absences indicated space group $P2_1/n$. The Rietveld method was used to refine the crystal structure, and the

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ca—O1$^{i}$ | 2.358 (5) | Ca—O2$^{ix}$ | 2.725 (5) |
| Ca—O2$^{ii}$ | 2.372 (5) | Ca—O3$^{x}$ | 3.136 (3) |
| Ca—O3$^{iii}$ | 2.345 (3) | Ca—O3$^{xi}$ | 3.217 (2) |
| Ca—O3$^{iv}$ | 2.431 (2) | Mg—O1 | 2.069 (3) |
| Ca—O1$^{v}$ | 2.624 (5) | Mg—O2$^{vii}$ | 2.077 (3) |
| Ca—O1$^{vi}$ | 2.675 (5) | Mg—O3$^{xii}$ | 2.057 (4) |
| Ca—O1$^{iv}$ | 3.396 (5) | W—O1$^{i}$ | 1.925 (3) |
| Ca—O2$^{vii}$ | 2.591 (5) | W—O2$^{vii}$ | 1.929 (3) |
| Ca—O2$^{viii}$ | 3.385 (5) | W—O3 | 1.913 (4) |
| | | | |
| O1—Mg—O2$^{vii}$ | 89.9 (2) | O1$^{i}$—W—O2$^{vii}$ | 89.4 (2) |
| O1—Mg—O3$^{xii}$ | 88.4 (2) | O1$^{i}$—W—O3$^{x}$ | 89.4 (2) |
| O2$^{vii}$—Mg—O3$^{xii}$ | 91.6 (2) | O2$^{vii}$—W—O3$^{x}$ | 90.6 (2) |

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

X-ray and neutron profiles were simultaneously fitted by the *FULLPROF*2000 program (Rodríguez-Carvajal, 2001). The initial parameters for the refinement were taken from the data for the isomorphous compound $Sr_2YbNbO_6$, and atomic displacement parameters were assumed to be isotropic.

For both compounds, data collection: Rigaku Rotaflex software; cell refinement: *FULLPROF*2000 (Rodríguez-Carvajal, 2001); data reduction: *FULLPROF*2000; program(s) used to solve structure: *FULLPROF*2000; program(s) used to refine structure: *FULLPROF*2000; molecular graphics: *XtalDRAW* (Downs *et al.*, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1029). Services for accessing these data are described at the back of the journal.

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