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Supporting information for article:

Octahedral tilting in the tungsten bronzes

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Isotropy, Version 9.3.1, June 2013
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DISPLAY SETTING
Current setting is International (new ed.) with conventional basis vectors.
DISPLAY SETTING IRREP
Current irrep version is 2011
Use "VALUE IRREP VERSION" to change version
*value parent 191
*value Wyckoff f
*value irrep l2-
*value direction p3
*show irrep
*show microscopic vector pseudo
*display distortion
Irrep (ML) Point       Projected Pseudo Vectors
L2-        (1/2,0,0)   (0,0,0)
           (1/2,0,1)   (0,0,0)
           (1/2,1,0)   (2,0,0)
           (1/2,1,1)   (-2,0,0)
           (3/2,0,0)   (0,0,0)
           (3/2,0,1)   (0,0,0)
           (3/2,1,0)   (-2,0,0)
           (3/2,1,1)   (2,0,0)
           (1/2,1/2,0) (0,0,0)
           (1/2,1/2,1) (0,0,0)
           (1/2,3/2,0) (-2,-2,0)
           (1/2,3/2,1) (2,2,0)
           (3/2,1/2,0) (2,2,0)
           (3/2,1/2,1) (-2,-2,0)
           (3/2,3/2,0) (0,0,0)
           (3/2,3/2,1) (0,0,0)
           (0,1/2,0)   (0,0,0)
           (0,1/2,1)   (0,0,0)
           (0,3/2,0)   (0,0,0)
           (0,3/2,1)   (0,0,0)
           (1,1/2,0)   (0,-2,0)
           (1,1/2,1)   (0,2,0)
           (1,3/2,0)   (0,2,0)
           (1,3/2,1)   (0,-2,0)
L2-        (1/2,0,0)   (1.155,2.309,0)
           (1/2,0,1)   (-1.155,-2.309,0)
           (1/2,1,0)   (0,0,0)
           (1/2,1,1)   (0,0,0)
           (3/2,0,0)   (-1.155,-2.309,0)
           (3/2,0,1)   (1.155,2.309,0)
           (3/2,1,0)   (0,0,0)
           (3/2,1,1)   (0,0,0)
           (1/2,1/2,0) (-1.155,1.155,0)
           (1/2,1/2,1) (1.155,-1.155,0)
           (1/2,3/2,0) (0,0,0)
           (1/2,3/2,1) (0,0,0)
           (3/2,1/2,0) (0,0,0)
           (3/2,1/2,1) (0,0,0)
           (3/2,3/2,0) (1.155,-1.155,0)
           (3/2,3/2,1) (-1.155,1.155,0)
           (0,1/2,0)   (-2.309,-1.155,0)
           (0,1/2,1)   (2.309,1.155,0)
           (0,3/2,0)   (2.309,1.155,0)
           (0,3/2,1)   (-2.309,-1.155,0)
           (1,1/2,0) (0,0,0)
           (1,1/2,1) (0,0,0)
           (1,3/2,0) (0,0,0)
           (1,3/2,1) (0,0,0)
*show parent
*show subgroup
*show origin
*show basis
*display isotropy
Parent     Irrep (ML) Subgroup   Basis Vectors           Origin
191 P6/mmm L2-        191 P6/mmm (2,0,0),(0,2,0),(0,0,2) (0,0,1/2)
*quit
```

Figure S1 HTB: examination of the tilting associated with irrep L_2^-. The two independent modes are added in equal measures to give the acceptable tilt system illustrated at Fig. S2. The structure obtained retains the parent space group symmetry *P*6/*mmm* but is on a doubled cell.

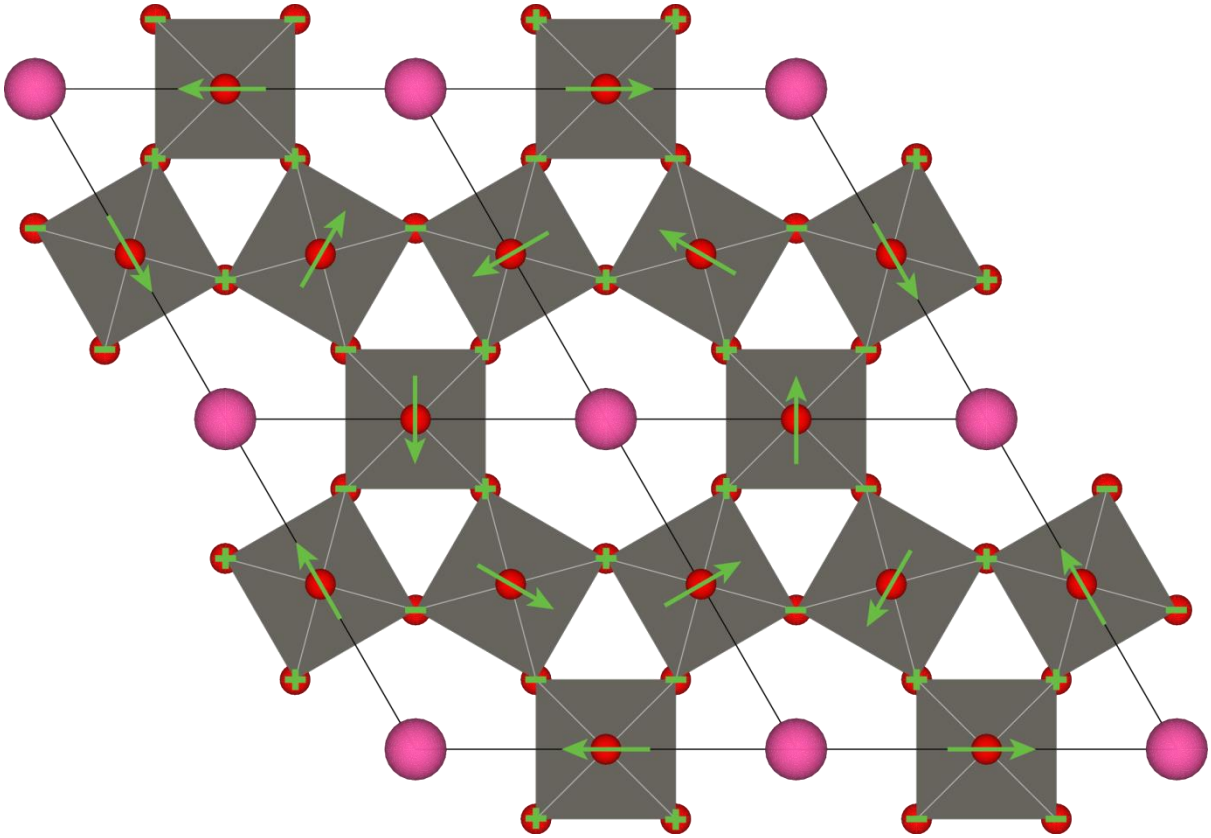

Figure S2 HTB: illustration of the tilt system associated with L_2^-. The structure and the tilts are indicated in the same manner as at Fig. 1.

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DISPLAY SETTING
Current setting is International (new ed.) with conventional basis vectors.
DISPLAY SETTING IRREP
Current irrep version is 2011
Use "VALUE IRREP VERSION" to change version
*value parent 127
*value Wyckoff d
*value irrep s3
*value kvalue 1,1/4
*value direction p1
*show irrep
*show microscopic vector pseudo
*display distortion
Irrep (ML) Point      Projected Pseudo Vectors
S3         (0,1/2,0)  (0,0,0)
           (0,-1/2,1) (0,0,0)
           (0,1/2,1)  (0,0,0)
           (1,1/2,1)  (0,0,0)
           (1/2,0,0)  (-1,1,0)
           (1/2,-1,1) (1,-1,0)
           (1/2,0,1)  (1,-1,0)
           (3/2,0,1)  (-1,1,0)
S3         (0,1/2,0)  (1,-1,0)
           (0,-1/2,1) (-1,1,0)
           (0,1/2,1)  (-1,1,0)
           (1,1/2,1)  (1,-1,0)
           (1/2,0,0)  (0,0,0)
           (1/2,-1,1) (0,0,0)
           (1/2,0,1)  (0,0,0)
           (3/2,0,1)  (0,0,0)
*show parent
*show subgroup
*show basis
*show origin
*display isotropy
Parent     Irrep (ML) Subgroup Basis Vectors              Origin
127 P4/mbm S3         63 Cmcm  (0,0,2),(-2,-2,0),(1,-1,0) (1/2,1/2,1/2)
*quit
```

Figure S3 TTB: examination of the tilting associated with irrep *S*3 at *a*=1/4 on the *S*-line of symmetry, ***k***=*a*,*a*,1/3. The two independent modes are added in equal measure to give the acceptable tilt system illustrated at Fig. S4. The structure obtained has space group setting *Cmcm* (standard setting); it can be shown alternatively as in *Bbmm* on a 2√2 by √2 by 2 unit cell.

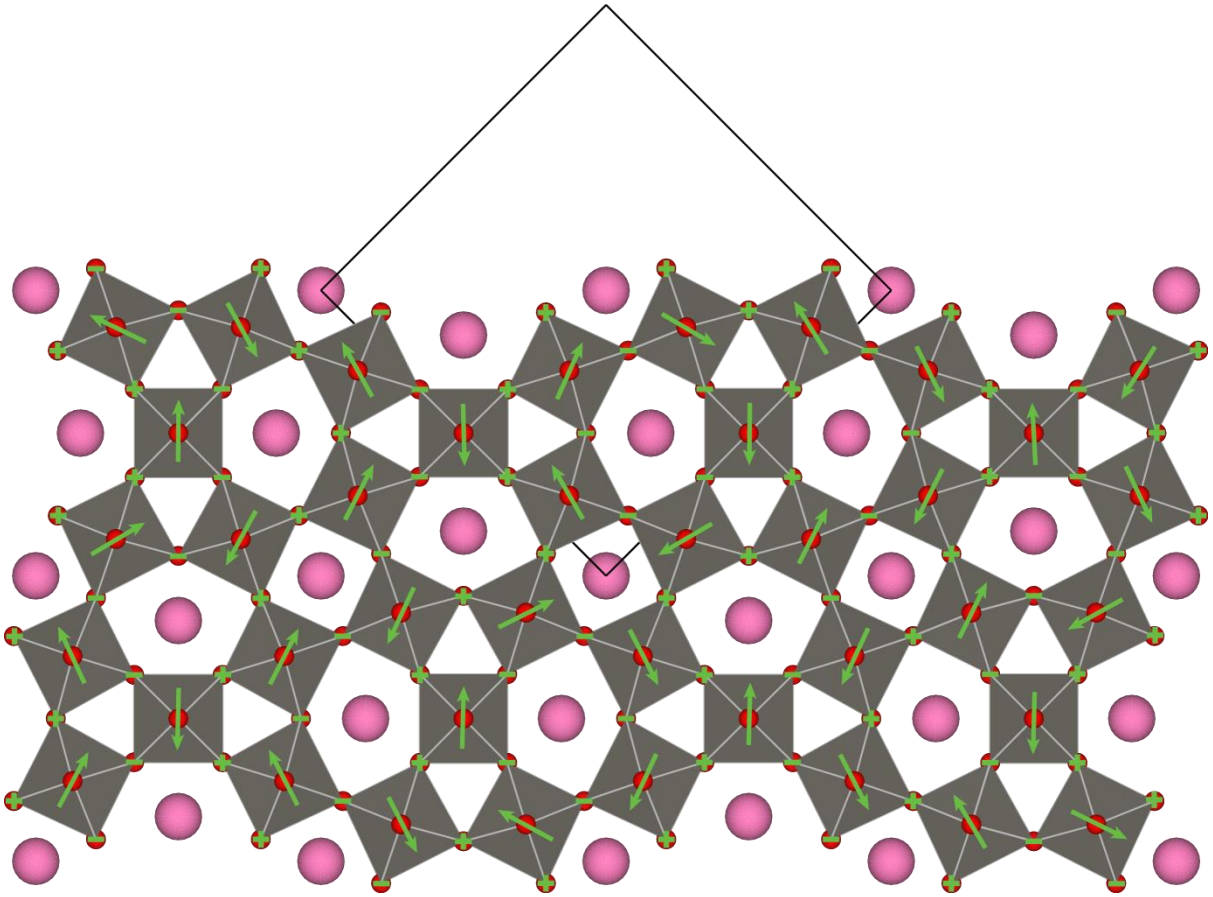

Figure S4 TTB: illustration of an acceptable tilt system associated with irrep *S*3. The structure and the tilts are indicated in the same manner as at Fig. 4.

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DISPLAY SETTING
Current setting is International (new ed.) with conventional basis vectors.
DISPLAY SETTING IRREP
Current irrep version is 2011
Use "VALUE IRREP VERSION" to change version
*value parent 127
*value irrep gm3-
*value Wyckoff d I
*show microscopic vector
*show Wyckoff
*show irrep
*display distortion
Irrep (ML) Wyckoff Point              Projected Vectors
GM3-       d       (0,1/2,0)          (0,0,1)
                   (1/2,0,0)          (0,0,1)
GM3-       i       (x,y,0)            (0,0,1)
                   (x+1/2,-y+1/2,0)   (0,0,1)
                   (-x+1/2,y+1/2,0)   (0,0,1)
                   (-x,-y,0)          (0,0,1)
                   (-y+1/2,-x+1/2,0)  (0,0,1)
                   (-y,x,0)           (0,0,1)
                   (y,-x,0)           (0,0,1)
                   (y+1/2,x+1/2,0)    (0,0,1)
*quit
```

Figure S5 TTB: confirmation that irrep Γ^{-}_{3} leads to displacements in the *z*-direction of the ions (Nb, say) located at Wyckoff *d* and *i*.

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DISPLAY SETTING
Current setting is International (new ed.) with conventional basis vectors.
DISPLAY SETTING IRREP
Current irrep version is 2011
Use "VALUE IRREP VERSION" to change version
*value parent 127
*value irrep gm3-
*show parent
*show subgroup
*show basis
*show origin
*show continuous
*display isotropy
Parent     Subgroup Cont Basis Vectors           Origin
127 P4/mbm 100 P4bm RG   (1,0,0),(0,1,0),(0,0,1) (0,0,0)
*value irrep a5- gm3-
*value direction p1(1)p1(1)
*display isotropy coupled
Parent     Subgroup Basis Vectors              Origin
127 P4/mbm 79 I4    (-1,1,0),(-1,-1,0),(0,0,2) (0,0,0)
*value irrep s3 gm3-
*value kvalue 1,1/4 0,0
*value direction p1(1)p1(1)
*display isotropy coupled
Adding coupled isotropy subgroups...
Parent     Subgroup Basis Vectors               Origin
127 P4/mbm 40 Ama2  (1,-1,0),(-2,-2,0),(0,0,-2) (1/2,1/2,1/2)
*quit
```

Figure S6 **TTB:** the structures resulting when distortions associated with irrep Γ_3^- are included.

The structure in *Ama2* on a √2 by 2√2 by 2 cell can be reset in *Bbm2* on a 2√2 by √2 by 2 unit cell.