SUPPORTING DOCUMENTATION

APPENDIX 1 Structural data, reciprocal lattice vectors and their labeling for *seifertite*, *stishovite*, *coesite* and *rutile* used in the present study.

a. *Seifertite*

Seifertite, space group 60 Pbcn, has the structure shown in Figure A1-1.

Figure A1-1

Figure A1-1 Unit cell of *seifertite.* Values of primitive translations a, b, c in the x, y, z directions and fractional coordinates of Si and O are given in the text. The coordination of Si by O is nearly octahedral and that of O by Si is trigonal.

Lattice constants and fractional coordinates are from Dera et al. (2002).

The primitive translation vectors of its orthorhombic cell ($\boldsymbol{a,b,c}$) ≡ (a $\hat{x}$, b $\hat{y}$, c $\hat{z}$) are

a = 7.742210 bohr,
b = 9.528000 bohr,
c = 8.493570 bohr,

The unit cell contains 4 SiO_2 formula units with 4 equivalent Si atoms and 8 O atoms at fractional coordinates of the unique atoms

Si (0.0000, 0.1522, 0.2500),
O (0.7336, 0.6245, 0.9186),

the rest being generated by the symmetry operations of the Pbcn group as in the Birkbeck College University of London (1997-1999) space group database. The space group Pb2n given by El Goresy et al. (2008) as an alternative was not used, since satisfactory results were obtained with the higher symmetry Pbcn group.

The reciprocal lattice is also orthorhombic, formed by the vectors ($\boldsymbol{a^*, b^*, c^*}$) such that

$\boldsymbol{a^*} = 2\pi(\boldsymbol{b} \times \boldsymbol{c})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.811549\ \hat{x}\ \text{bohr}^{-1}$,
$\boldsymbol{b^*} = 2\pi(\boldsymbol{c} \times \boldsymbol{a})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.659444\ \hat{y}\ \text{bohr}^{-1}$,
$\boldsymbol{c^*} = 2\pi(\boldsymbol{a} \times \boldsymbol{b})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.739758\ \hat{z}\ \text{bohr}^{-1}$

as shown in Figure A1-2.

Figure A1-2

Figure A1-2 Brillouin zone of the orthorhombic lattice. Critical points chosen for the band structure representation are labeled as Γ (0,0,0), Z (0,0, ½), R (½, ½, ½), S (½, ½,0), X (½,0,0), U (½,0, ½). Lengths of the reciprocal vectors a*, b*, c* are in the ratio generated by the *seifertite* structure.

b. *Stishovite*

Stishovite, space group 136 P42/mnm, has the structure shown in Figure A1-3.

Figure A1-3

Figure A1-3 Unit cell of *stishovite.* Values of primitive translations a, b, c in the x, y, z directions and fractional coordinates of Si and O are given in the text. The coordination of Si by O is nearly octahedral and that of O by Si is trigonal.

Lattice constants and fractional coordinates are from Rudra and Fowler (1983).

The primitive translation vectors of its tetragonal cell (***a,b,c***) ≡ (a $\hat{x}$, a $\hat{y}$, c $\hat{z}$) are

a = 7.893770 bohr,
b = 7.893770 bohr,
c = 5.036310 bohr,

The unit cell contains 2 SiO_2 formula units with fractional coordinates of the Si and O atoms

Si (1) (0.0000, 0.0000, 0.0000),
Si (2) (0.5000, 0.5000, 0.5000),
O (3) (0.3062, 0.3062, 0.0000),
O (4) (0.6938, 0.6938, 0.0000),
O (5) (0.1938, 0.8062, 0.5000),
O (6) (0.8062, 0.1938, 0.5000),

generated from unique positions of Si(1) and O(3) by the symmetry operations of the P42/mnm group.

The reciprocal lattice is also tetragonal, formed by the vectors (***a*, b*, c****) such that

$\boldsymbol{a}^* = 2\pi(\boldsymbol{b} \times \boldsymbol{c})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.795968\ \hat{x}\ \text{bohr}^{-1}$,
$\boldsymbol{b}^* = 2\pi(\boldsymbol{c} \times \boldsymbol{a})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.795968\ \hat{y}\ \text{bohr}^{-1}$,

$\boldsymbol{c^*} = 2\pi(\boldsymbol{a} \times \boldsymbol{b})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 1.247577\ \hat{z}\ \text{bohr}^{-1}$

shown in Figure A1-4 with labeling of the special points consistent with that that of Rudra and Fowler (1983).

Figure A1-4

Figure A1-4 Brillouin zone of the tetragonal lattice. Critical points chosen for the band structure representation are labeled as Γ (0,0,0), Z (0,0, ½), A (½, ½, ½), M (½, ½,0), X (½,0,0), R (½,0, ½). Intermediate points Λ, S, V, Σ, Δ, W and U have coordinates specified in the klist_band for the tetragonal lattice. Lengths of the reciprocal vectors a*, b*, c* are in the ratio yielded by the *stishovite* structure.

c. Coesite

Coesite, space group 15 C2/c, has the structure shown in Figure A1-5.

Figure A1-5

Figure A1-5 Unit cell of *coesite* as a stereo picture. Values of primitive translations a, b, c in the x, y, z directions and fractional coordinates of Si and O are given in the text. The coordination of Si by O is tetrahedral and that of O by Si is two-fold. O atoms at (0,0,0) and (1/2,1/2,1/2) are linearly coordinated to the nearest two Si neighbors, a feature that has influence on distribution of levels in the valence band.

Lattice constants and fractional coordinates are taken from single crystal neutron diffraction data at 292 K by Smyth et al. (1987).

The primitive translation vectors of its monoclinic cell $(\boldsymbol{a,b,c}) \equiv (a\ \hat{x}, b\ \hat{y}, c1\ \hat{x} + c2\ \hat{z})$ are

a = 13.4845 bohr,
b = 23.4014 bohr,
c1 = -6.8665 bohr,
c2 =11.7154 bohr,

and the angle subtended by vectors $\boldsymbol{a}$ and $\boldsymbol{c}$ is $\beta = 120.375^{o}$.

The unit cell contains 16 SiO_2 formula units with two Si and five O unique atoms at fractional coordinates

Si(1) (0.14032, 0.10832, 0.07231) multiplicity 4,
Si(2) (0.50677, 0.15800, 0.54073) multiplicity 4,

O(1) (0.00000, 0.00000, 0.00000) multiplicity 2,
O(2) (0.50000, 0.11643, 0.75000) multiplicity 2,
O(3) (0.26631, 0.12320, 0.94031) multiplicity 4,
O(4) (0.31144, 0.10379, 0.32785) multiplicity 4,
O(5) (0.01746, 0.21192, 0.47851) multiplicity 4,

the rest being generated by the symmetry operations of the C2/c group[29].

The reciprocal lattice is also monoclinic, formed by the vectors (***a*, b*, c****) such that

$\boldsymbol{a^*} = 2\pi(\boldsymbol{b} \times \boldsymbol{c})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = (0.465956\ \hat{x} + 0.273102\ \hat{z})$ bohr^{-1},
$\boldsymbol{b^*} = 2\pi(\boldsymbol{c} \times \boldsymbol{a})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.268496\ \hat{y}$ bohr^{-1},
$\boldsymbol{c^*} = 2\pi(\boldsymbol{a} \times \boldsymbol{b})/[\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c})] = 0.536318\ \hat{z}$ bohr^{-1},

shown in Figure A1-6 with special points generated with the help of the Xcrysden program, Kokalj (2003).
The angles between the reciprocal lattice vectors are $\sphericalangle(\boldsymbol{a^*}, \boldsymbol{c^*}) = 59.625^o$ and $\sphericalangle(\boldsymbol{a^*}, \boldsymbol{b^*}) = \sphericalangle(\boldsymbol{b^*}, \boldsymbol{c^*}) = 90^o$. and lengths of the reciprocal vectors a*, b*, c* are in the ratio created by the *coesite* structure. The coesite structure in this representation is close to hexagonal about the principal axis ***b***.

Figure A1-6

Figure A1-6 Brillouin zone of the monoclinic, nearly hexagonal lattice about the b* axis.
Critical points chosen for the band structure representation are labeled as:
Γ (0,0,0), K2 (0, ½, 0), K3 (0.335, ½, 0.33), K4 (0.335,0, 0.33), K5 = Γ, K6 (½,0,0), K7 (½,½,0), K8 = K2.
The corresponding labels for the idealized hexagonal lattice are:
Γ ≡ [K1 = K5], A ≡ [K2 = K8], H ≡ K3, K ≡ K4, M ≡ K6 and L ≡ K7

Wien 2k structure files of *seifertite, stishovite, coesite* and *rutile*

Seifertite

```
P   LATTICE,NONEQUIV. ATOMS  2                          60 Pbcn

MODE OF CALC=RELA

  7.742210  9.528000  8.493570 90.000000 90.000000 90.000000

ATOM  -1: X=0.00000000 Y=0.15220000 Z=0.25000000

          MULT= 4          ISPLIT= 8
```

```
      -1: X=0.00000000 Y=0.84780000 Z=0.75000000

      -1: X=0.50000000 Y=0.65220000 Z=0.25000000

      -1: X=0.50000000 Y=0.34780000 Z=0.75000000

Si1        NPT=  781  R0=0.00010000 RMT=    1.6000   Z: 14.0

LOCAL ROT MATRIX:    0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000

                     1.0000000 0.0000000 0.0000000

ATOM  -2: X=0.73360000 Y=0.62450000 Z=0.91860000

          MULT= 8          ISPLIT= 8

      -2: X=0.26640000 Y=0.37550000 Z=0.08140000

      -2: X=0.23360000 Y=0.12450000 Z=0.58140000

      -2: X=0.76640000 Y=0.87550000 Z=0.41860000

      -2: X=0.76640000 Y=0.12450000 Z=0.91860000

      -2: X=0.23360000 Y=0.87550000 Z=0.08140000

      -2: X=0.26640000 Y=0.62450000 Z=0.58140000

      -2: X=0.73360000 Y=0.37550000 Z=0.41860000

O 2        NPT=  781  R0=0.00010000 RMT=    1.6000   Z:  8.0

LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000

                     0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000

8 symmetry operations are auto-generated by the Pbcn group
```

Stishovite

```
P   LATTICE,NONEQUIV. ATOMS  2                   136 P42/mnm

MODE OF CALC=RELA

  7.893770  7.893770  5.036310 90.000000 90.000000 90.000000

ATOM  -1: X=0.00000000 Y=0.00000000 Z=0.00000000

          MULT= 2          ISPLIT= 8

      -1: X=0.50000000 Y=0.50000000 Z=0.50000000

Si         NPT=  781  R0=0.00010000 RMT=    1.6500   Z: 14.0

LOCAL ROT MATRIX:    0.7071068 0.7071068 0.0000000

                    -0.7071068 0.7071068 0.0000000

                     0.0000000 0.0000000 1.0000000

ATOM  -2: X=0.30620000 Y=0.30620000 Z=0.00000000

          MULT= 4          ISPLIT= 8

      -2: X=0.69380000 Y=0.69380000 Z=0.00000000

      -2: X=0.19380000 Y=0.80620000 Z=0.50000000

      -2: X=0.80620000 Y=0.19380000 Z=0.50000000

O 1        NPT=  781  R0=0.00010000 RMT=    1.6500   Z:  8.0

LOCAL ROT MATRIX:    0.0000000-0.7071068 0.7071068

                     0.0000000 0.7071068 0.7071068

                    -1.0000000 0.0000000 0.0000000
```

16 symmetry operations are auto-generated by the P42/mnm group

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Coesite

P   LATTICE,NONEQUIV. ATOMS 7

MODE OF CALC=RELA

 13.484500 23.401400 13.579400 90.000000120.375000 90.000000

ATOM -1: X=0.13998000 Y=0.10847000 Z=0.07211000

          MULT= 4   ISPLIT= 8

      -1: X=0.86002000 Y=0.89153000 Z=0.92789000

      -1: X=0.86002000 Y=0.10847000 Z=0.42789000

      -1: X=0.13998000 Y=0.89153000 Z=0.57211000

Si1   NPT= 781 R0=0.00010000 RMT=   1.4900   Z= 14.0

LOCAL ROT MATRIX: 1.0000000 0.0000000 0.0000000

                     0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000

ATOM -2: X=0.50722000 Y=0.15785000 Z=0.54153000

          MULT= 4   ISPLIT= 8

      -2: X=0.49278000 Y=0.84215000 Z=0.45847000

```
      -2: X=0.49278000 Y=0.15785000 Z=0.95847000

      -2: X=0.50722000 Y=0.84215000 Z=0.04153000

Si2        NPT=  781  R0=0.00010000 RMT=    1.4900   Z= 14.0

LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000

                     0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000

ATOM  -3: X=0.00000000 Y=0.00000000 Z=0.00000000

          MULT= 2          ISPLIT= 8

      -3: X=0.00000000 Y=0.00000000 Z=0.50000000

O 1        NPT=  781  R0=0.00010000 RMT=    1.4900   Z=  8.0

LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000

                     0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000

ATOM  -4: X=0.50000000 Y=0.11524000 Z=0.75000000

          MULT= 2          ISPLIT= 8

      -4: X=0.50000000 Y=0.88476000 Z=0.25000000

O 2        NPT=  781  R0=0.00010000 RMT=    1.4900   Z=  8.0

LOCAL ROT MATRIX:    0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000

                     1.0000000 0.0000000 0.0000000

ATOM  -5: X=0.26400000 Y=0.12452000 Z=0.93830000
```

```
           MULT= 4          ISPLIT= 8
      -5: X=0.73600000 Y=0.87548000 Z=0.06170000
      -5: X=0.73600000 Y=0.12452000 Z=0.56170000
      -5: X=0.26400000 Y=0.87548000 Z=0.43830000
O 3        NPT=  781  R0=0.00010000 RMT=    1.4900   Z=  8.0
LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000
                     0.0000000 1.0000000 0.0000000
                     0.0000000 0.0000000 1.0000000
ATOM  -6: X=0.31277000 Y=0.10319000 Z=0.32768000
           MULT= 4          ISPLIT= 8
      -6: X=0.68723000 Y=0.89681000 Z=0.67232000
      -6: X=0.68723000 Y=0.10319000 Z=0.17232000
      -6: X=0.31277000 Y=0.89681000 Z=0.82768000
O 4        NPT=  781  R0=0.00010000 RMT=    1.4900   Z=  8.0
LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000
                     0.0000000 1.0000000 0.0000000
                     0.0000000 0.0000000 1.0000000
ATOM  -7: X=0.01900000 Y=0.21178000 Z=0.47664000
           MULT= 4          ISPLIT= 8
      -7: X=0.98100000 Y=0.78822000 Z=0.52336000
      -7: X=0.98100000 Y=0.21178000 Z=0.02336000
```

```
      -7: X=0.01900000 Y=0.78822000 Z=0.97664000

O 5        NPT=  781  R0=0.00010000 RMT=    1.4900   Z=  8.0

LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000

                     0.0000000 1.0000000 0.0000000

                     0.0000000 0.0000000 1.0000000


4 symmetry operations are auto-generated by the C2/c group

-------------------------------------------------------------------------------------------------------------
```

Rutile – lattice constants from Ekuma and Bagayoko (2011), fractional coordinates as in stishovite

```
P   LATTICE,NONEQUIV. ATOMS  2                   136 P42/mnm

MODE OF CALC=RELA

  8.683743  8.683743  5.593006 90.000000 90.000000 90.000000

ATOM  -1: X=0.00000000 Y=0.00000000 Z=0.00000000

          MULT= 2          ISPLIT= 8

      -1: X=0.50000000 Y=0.50000000 Z=0.50000000

Ti         NPT=  781  R0=0.00005000 RMT=    1.9000   Z: 22.0

LOCAL ROT MATRIX:    0.7071068 0.7071068 0.0000000

                    -0.7071068 0.7071068 0.0000000

                     0.0000000 0.0000000 1.0000000

ATOM  -2: X=0.30620000 Y=0.30620000 Z=0.00000000
```

```
           MULT= 4          ISPLIT= 8

       -2: X=0.69380000 Y=0.69380000 Z=0.00000000

       -2: X=0.19380000 Y=0.80620000 Z=0.50000000

       -2: X=0.80620000 Y=0.19380000 Z=0.50000000

O 1        NPT=  781  R0=0.00010000 RMT=    1.7000   Z:  8.0

LOCAL ROT MATRIX:    0.0000000-0.7071068 0.7071068

                     0.0000000 0.7071068 0.7071068

                    -1.0000000 0.0000000 0.0000000

16 symmetry operations are auto-generated by the P42/mnm group
```

List of k-points for band structure rendition of *seifertite*, *stishovite*, *coesite* and *rutile*

***Seifertite*:**

```
GAMMA          0    0    0   12  2.0-8.00 8.00

               0    0    1   12  2.0

               0    0    2   12  2.0

               0    0    3   12  2.0

               0    0    4   12  2.0

               0    0    5   12  2.0

Z              0    0    8   16  2.0

               1    1    8   16  2.0

               2    2    8   16  2.0

               3    3    8   16  2.0
```

	4	4	8	16	2.0
	5	5	8	16	2.0
	6	6	8	16	2.0
	7	7	8	16	2.0
R	6	6	6	12	2.0
	6	6	5	12	2.0
	6	6	4	12	2.0
	6	6	3	12	2.0
	6	6	2	12	2.0
	6	6	1	12	2.0
S	8	8	0	16	2.0
	7	7	0	16	2.0
	6	6	0	16	2.0
	5	5	0	16	2.0
	4	4	0	16	2.0
	3	3	0	16	2.0
	2	2	0	16	2.0
	1	1	0	16	2.0
GAMMA	0	0	0	14	2.0
	1	0	0	14	2.0
	2	0	0	14	2.0

	3	0	0	14	2.0
	4	0	0	14	2.0
	5	0	0	14	2.0
	6	0	0	14	2.0
X	6	0	0	12	2.0
	6	0	1	12	2.0
	6	0	2	12	2.0
	6	0	3	12	2.0
	6	0	4	12	2.0
	6	0	5	12	2.0
U	7	0	7	14	2.0
	6	0	7	14	2.0
	5	0	7	14	2.0
	4	0	7	14	2.0
	3	0	7	14	2.0
	2	0	7	14	2.0
	1	0	7	14	2.0
Z	0	0	7	14	2.0

Stishovite and *Rutile*:

GAMMA	0	0	0	22	2.0-8.00 8.00
	0	0	1	22	2.0
	0	0	2	22	2.0
	0	0	3	22	2.0
	0	0	4	22	2.0
LAMBDA	0	0	5	22	2.0
	0	0	6	22	2.0
	0	0	7	22	2.0
	0	0	8	22	2.0
	0	0	9	22	2.0
	0	0	10	22	2.0
Z	0	0	10	20	2.0
	1	1	10	20	2.0
	2	2	10	20	2.0
	3	3	10	20	2.0
	4	4	10	20	2.0
S	5	5	10	20	2.0
	6	6	10	20	2.0
	7	7	10	20	2.0
	8	8	10	20	2.0

	9	9	10	20	2.0
A	11	11	11	22	2.0
	11	11	10	22	2.0
	11	11	9	22	2.0
	11	11	8	22	2.0
	11	11	7	22	2.0
V	11	11	6	22	2.0
	11	11	5	22	2.0
	11	11	4	22	2.0
	11	11	3	22	2.0
	11	11	2	22	2.0
	11	11	1	22	2.0
M	10	10	0	20	2.0
	9	9	0	20	2.0
	8	8	0	20	2.0
	7	7	0	20	2.0
	6	6	0	20	2.0
SIGMA	5	5	0	20	2.0
	4	4	0	20	2.0
	3	3	0	20	2.0
	2	2	0	20	2.0

	1	1	0	20	2.0
GAMMA	0	0	0	14	2.0
	1	0	0	14	2.0
	2	0	0	14	2.0
	3	0	0	14	2.0
DELTA	4	0	0	14	2.0
	5	0	0	14	2.0
	6	0	0	14	2.0
X	11	0	0	22	2.0
	11	0	1	22	2.0
	11	0	2	22	2.0
	11	0	3	22	2.0
	11	0	4	22	2.0
W	11	0	5	22	2.0
	11	0	6	22	2.0
	11	0	7	22	2.0
	11	0	8	22	2.0
	11	0	9	22	2.0
	11	0	10	22	2.0
R	7	0	7	14	2.0
	6	0	7	14	2.0

```
                5    0    7   14  2.0

                4    0    7   14  2.0

U               3    0    7   14  2.0

                2    0    7   14  2.0

                1    0    7   14  2.0

Z               0    0    7   14  2.0
```

***Coesite*:**

```
K.1             0    0    0 3822  2.0-8.00 8.00

                0  273    0 3822  2.0

                0  546    0 3822  2.0

                0  819    0 3822  2.0

                0 1092    0 3822  2.0

                0 1365    0 3822  2.0

                0 1638    0 3822  2.0

K.2             0 4095    0 8190  2.0

              183 4095  180 8190  2.0

              366 4095  360 8190  2.0

              549 4095  540 8190  2.0
```

	732	4095	720	8190	2.0
	915	4095	900	8190	2.0
	1098	4095	1080	8190	2.0
	1281	4095	1260	8190	2.0
	1464	4095	1440	8190	2.0
	1647	4095	1620	8190	2.0
	1830	4095	1800	8190	2.0
	2013	4095	1980	8190	2.0
	2196	4095	2160	8190	2.0
	2379	4095	2340	8190	2.0
	2562	4095	2520	8190	2.0
K.3	1281	1911	1260	3822	2.0
	1281	1638	1260	3822	2.0
	1281	1365	1260	3822	2.0
	1281	1092	1260	3822	2.0
	1281	819	1260	3822	2.0
	1281	546	1260	3822	2.0
	1281	273	1260	3822	2.0
K.4	2745	0	2700	8190	2.0
	2562	0	2520	8190	2.0
	2379	0	2340	8190	2.0

	2196	0	2160	8190	2.0
	2013	0	1980	8190	2.0
	1830	0	1800	8190	2.0
	1647	0	1620	8190	2.0
	1464	0	1440	8190	2.0
	1281	0	1260	8190	2.0
	1098	0	1080	8190	2.0
	915	0	900	8190	2.0
	732	0	720	8190	2.0
	549	0	540	8190	2.0
	366	0	360	8190	2.0
	183	0	180	8190	2.0
K.5	0	0	0	7098	2.0
	273	0	0	7098	2.0
	546	0	0	7098	2.0
	819	0	0	7098	2.0
	1092	0	0	7098	2.0
	1365	0	0	7098	2.0
	1638	0	0	7098	2.0
	1911	0	0	7098	2.0
	2184	0	0	7098	2.0

	2457	0	0	7098	2.0
	2730	0	0	7098	2.0
	3003	0	0	7098	2.0
	3276	0	0	7098	2.0
K.6	1911	0	0	3822	2.0
	1911	273	0	3822	2.0
	1911	546	0	3822	2.0
	1911	819	0	3822	2.0
	1911	1092	0	3822	2.0
	1911	1365	0	3822	2.0
	1911	1638	0	3822	2.0
K.7	3549	3549	0	7098	2.0
	3276	3549	0	7098	2.0
	3003	3549	0	7098	2.0
	2730	3549	0	7098	2.0
	2457	3549	0	7098	2.0
	2184	3549	0	7098	2.0
	1911	3549	0	7098	2.0
	1638	3549	0	7098	2.0
	1365	3549	0	7098	2.0
	1092	3549	0	7098	2.0

```
              819 3549    0 7098  2.0

              546 3549    0 7098  2.0

              273 3549    0 7098  2.0

K.8             0 3549    0 7098  2.0
```

APPENDIX 2 Comparison of band structures of *α-quartz* in the GW approximation (A2-1) and using the mBJ potential with spin polarization and self-interaction correction for the Si3d orbitals (A2-2). Experimental bandgap obtained by low-loss measurement in EELS/TEM is 9.65 eV from Garvie et al. (2000).

A2-1: GW method from Chang et al. (2000):

Figure A2-1

Figure A2-1. Calculated quasiparticle band structure of *α-quartz* in the GW approximation.

A2-2. Present mBJ method:

Figure A2-2

Figure A2-2. Calculated band structure of *α-quartz* in the mBJ/spin-polarized/Si3d-FLL approximation.
The two approaches yield very similar band structures of *α*-quartz and a very good account for the bandgap. Experimental gap energy is 9.65 eV, Γ→Γ gap is 10.1 eV calculated by the GW approximation and 9.41 eV in the present work using the mBJ approximation.

APPENDIX 3 Partial DOS in the VBs of *coesite, α-quartz, stishovite and seifertite.*

Partial DOS graphs presented here reveal the causes of occurrence of intra-VB gap in silica polymorphs with tetrahedrally coordinated Si. Figure A3-1 shows conditions prevailing in *coesite*, Figure A3-2 those in *α-quartz*, Figure A3-3 in *stishovite* and Figure A3-4 in *seifertite*.

Common features of the two tetrahedral polymorphs *coesite* and *α-quartz* are: (a) low contributions of Si to the split-off upper portion of VB; (b) significant contributions of Si to the split-off lower portion of VB; and (c) overlap of Si and O contributions in the lower VB indicating covalent Si-O bonding (Figures A3-1 and A3-2).

Figure A3-1

Figure A3-1 Partial VB DOS of Si and O contributions in *coesite*, showing a separation of ionic O2p band from covalent Si-O band across a 1.3 eV intrinsic gap.

Figure A3-2

Figure A3-2 Partial VB DOS of Si and O contributions in *α-quartz*, showing a separation of ionic O2p band from covalent Si-O band across a 1.7 eV intrinsic gap.

Common features of the two octahedral polymorphs *stishovite* and *seifertite* entail continuous, predominantly O2p valence bands with small, progressively decreasing contributions of Si from the bottom to the top of the VB (Figures A3-3 and A3-4).

Figure A3-3

Figure A3-3 Partial VB DOS of Si and O contributions in *stishovite*, showing a continuous band dominated by O2p orbitals with small contribution of Si orbitals decreasing from the bottom to the top of VB.

Figure A3-4

Figure A3-4 Partial VB DOS of Si and O contributions in *seifertite*, showing features similar to those of the *stishovite* VB in Figure A3-3.