A Chemical Pressure-Induced Phase Transition Controlled by Lone Electron Pair Activity

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1.-Computational details

a) General Aspects

The structural, electronic properties and EOS of crystalline SnMoO$_4$ and SnWO$_4$ pure compounds were evaluated under the periodic DFT framework using the CRYSTAL17 package.$^{1,2}$ To study the influence of different approximations for exchange and correlation contributions to the DFT energy, a complete structure optimization by using the HSE06$^{3,4}$ and B3LYP$^5$ functionals has been performed.

The atoms were described using pseudopotential basis sets: tungsten was described by a large-core ECP, derived by Hay and Wadt and modified by Cora et al.,$^6$ molybdenum by Mo-976-311 (d631)G,$^7$ tin by Sn_ECP28MDF-411(51d) G,$^8$ and oxygen by O_6-31d1G (all-electron).$^9$ The accuracy of the evaluation of the Coulomb and exchange series was controlled by five thresholds, whose adopted values were 10$^{-7}$ (overlap threshold for Coulomb integrals), 10$^{-7}$ (penetration threshold for Coulomb integrals), 10$^{-7}$ (overlap threshold for HF exchange integrals), 10$^{-7}$ and 10$^{-14}$ (pseudo-overlap for HF exchange series), which assure a convergence in total energy better than 10$^{-7}$ Hartree in all cases. The percent of Fock/Kohn–Sham matrices mixing has been set to 40 (IPMIX= 40).

The CRYSTAL program can perform an automatic scan over the volume to compute energy $E$ versus volume $V$ data that are then described by the third-order Birch–Murnaghan (BM-3) EOS.$^{10,11}$ For each volume, a full $V$-constrained geometry optimization was performed. As a result, the pressure dependence of the unit cell structure was determined, as well as the volume/pressure dependence of the total energy and enthalpy. In addition, an automatic scheme for computing the quasi-harmonic approximation (QHA) crystal properties has been used, considering a volume range extending from a $-3\%$ compression to a $+6\%$ expansion around the equilibrium unit cell volume. The band structures and projected densities of states (DOS) on atoms and orbitals were performed to analyze the electronic structure.

Electron Localization Function (ELF) and Crystal Orbital Hamilton Population (COHP) analysis were obtained from single point calculations using VASP$^{12,13}$ at the optimized unit cell obtained from HSE06 CRYSTAL calculations. In this VASP calculations, we used the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional$^{14}$ and $k$-point gamma-centered Monkhorst-Pack meshes with a reciprocal spacing of $2\pi \times 0.1$ Å$^{-1}$. A kinetic energy cutoff of 600 eV for the plane wave basis set expansion was used to solve Kohn–Sham equations. The pseudopotentials utilized for Mo, W Sn and O atoms were standard projector-augmented wave pseudopotentials$^{15}$ provided in VASP code. The valence electrons considered for each atomic species are Mo (4s$^2$ 4p$^6$ 4d$^5$ 5s$^1$), W (5s$^2$ 5p$^6$ 5d$^4$ 6s$^2$), Sn (4d$^{10}$5s$^2$5p$^2$) and O (2s$^2$ 2s$^2$). COHP and the negative of the COHP integrated to the Fermi level were calculated by using the LOBSTER package.$^{16,17}$ PbeVaspFit2015 atomic basis were used to project the plane waves as implemented in the LOBSTER code. Specifically, the following atomic orbitals for each atomic species were used: O 2s 2p, Sn 4d 4p 4s 5p 5s, W 5d 5p 5s 6s and Mo 4d 4p 4s 5s.
b) Solid Solutions

In both structures (α and β), the number of formula units is $Z=4$. If one, two or three of the Mo positions are replaced by one, two or three W atoms, a 25%, 50% or 75% of substitution will be obtained. In the case of a 50% replacement, there are 3 different possibilities concerning the relative positions of the Mo and W atoms in the unit cell. We have computed all of them and selected the most energetically favorable.

The replacement of the Mo by W atoms implies a decrease of the cell parameters, except for the $b$ parameter which tend to increase for the α solid solution. However, when the substitution occurs with the solid solution containing half of the substituted W and Mo atoms in the β solid solution ($\beta\text{-SnW}_{0.50}\text{Mo}_{0.50}\text{O}_4$), the cubic parameter presents an orthorhombic distortion with values of 7.089, 7.102 and 7.110 Å. The substitution process of W by Mo cations induces variations in the atomic coordinates of the neighbor oxygen anions, indicating the existence of structural and electronic distortions in the local coordination of these cations.

2.- Results

Table S1. Optimized lattice parameters (Å) and band gap energy ($E_{\text{gap}}$, eV) of $\beta\text{-SnMoO}_4$, $\beta\text{-SnWO}_4$, $\alpha\text{-SnWO}_4$ and $\alpha\text{-SnMoO}_4$ along with the differences (%) with respect to the experimental values.

|            | $\beta\text{-SnMoO}_4$ | $\beta\text{-SnWO}_4$ | $\alpha\text{-SnWO}_4$ | $\alpha\text{-SnMoO}_4$ |
|------------|------------------------|------------------------|------------------------|------------------------|
|            | $a=b=c$ $E_{\text{gap}}$ | $a=b=c$ $E_{\text{gap}}$ | $a$ $b$ $c$ $E_{\text{gap}}$ | $a$ $b$ $c$ $E_{\text{gap}}$ |
| **B3LYP**  | 7.26 3.94             | 7.16 4.78             | 5.75 10.42 5.68 2.65 | 5.81 10.42 5.74 1.80 |
| Differences (%) | 0 --            | -1.78 78.36            | 2.31 -10.48 13.83 61.58 | 3.38 -10.48 15.03 |
| **HSE06**  | 7.13 3.37             | 7.07 4.15             | 5.61 10.57 5.50 2.14 | 5.60 10.72 5.42 1.34 |
| Differences (%) | -1.80 --          | -3.01 55.22            | -0.35 -9.19 10.22 30.48 | -0.35 -7.99 8.62 |
| **Experimental Reference** | 7.26$^{[19]}$ --$^{[1]}$ | 7.29$^{[18]}$ 2.68$^{[18]}$ | 5.62$^{[18]}$ 11.64$^{[18]}$ 4.99$^{[18]}$ 1.64$^{[18]}$ | 5.62$^{[18]}$ 11.64$^{[18]}$ 4.99$^{[18]}$ |
| **Theoretical Reference** | 7.54$^{[19]}$ 3.74$^{[19]}$ | 7.39$^{[18]}$ 3.45$^{[18]}$ | 5.59$^{[18]}$ 11.69$^{[18]}$ 4.99$^{[18]}$ 1.65$^{[18]}$ |
Table S2. Optimized lattice parameters of the α and β structures of the SnMo_{1-x}W_xO_4 (x = 0, 0.25, 0.50, 0.75, and 1) solid solutions along with calculated EOS parameters and band gap values.

| α-Phase | SnWO_4 | SnW_{0.75}Mo_{0.25}O_4 | SnW_{0.50}Mo_{0.50}O_4 | SnW_{0.25}Mo_{0.75}O_4 | SnMoO_4 |
|---------|--------|------------------------|------------------------|------------------------|---------|
| a (Å)   | 5.605  | 5.600                  | 5.597                  | 5.590                  | 5.597   |
| b (Å)   | 10.574 | 10.582                 | 10.610                 | 10.691                 | 10.717  |
| c (Å)   | 5.498  | 5.487                  | 5.469                  | 5.427                  | 5.423   |
| V (Å³)  | 325.94 | 325.22                 | 324.83                 | 324.10                 | 325.45  |
| B₀ (GPa)| 69.47  |                        |                        |                        | 57.60   |
| B’₀     | 4.98   |                        |                        |                        | 5.33    |
| Egap (eV)| 2.14   | 1.61                   | 1.38                   | 1.39                   | 1.34    |

| β-Phase | SnWO_4 | SnW_{0.75}Mo_{0.25}O_4 | SnW_{0.50}Mo_{0.50}O_4 | SnW_{0.25}Mo_{0.75}O_4 | SnMoO_4 |
|---------|--------|------------------------|------------------------|------------------------|---------|
| a (Å)   | 7.073  | 7.076                  | 7.089                  | 7.115                  | 7.131   |
| b (Å)   | 7.073  | 7.076                  | 7.102                  | 7.115                  | 7.131   |
| c (Å)   | 7.073  | 7.076                  | 7.110                  | 7.115                  | 7.131   |
| V (Å³)  | 353.97 | 353.15                 | 357.89                 | 360.21                 | 362.64  |
| B₀ (GPa)| 40.80  |                        |                        |                        | 41.93   |
| B’₀     | 7.22   |                        |                        |                        | 5.65    |
| Egap (eV)| 4.15   | 3.23                   | 3.22                   | 3.29                   | 3.37    |

Table S3. Optimized atomic positions in cartesian coordinates for the α and β structures of SnMo_{1-x}W_xO_4 (x = 0, 0.25, 0.50, 0.75, and 1) solid solutions.

α-SnMoO_4

|        | x           | y               | z               |
|--------|-------------|-----------------|-----------------|
| Sn     | 1.399582984 | 0               | 1.247593806     |
| Mo     | -1.534394528| 2.678618845     | 1.356430651     |
| O1     | 2.394477758 | 3.525203975     | -0.238585816    |
| O2     | 0.556428717 | 4.157763919     | -2.220641823    |

β-SnMoO_4

|        | x           | y               | z               |
|--------|-------------|-----------------|-----------------|
| Sn     | -1.003446067| -1.003446067    | -1.003446067    |
| Mo     | 1.149559561 | 1.149559561     | 1.149559561     |
| O1     | 2.188630691 | 2.188630691     | 2.188630691     |
| O2     | -0.912633084| -1.548230497    | -3.171277541    |

α-SnWO_4

|        | x           | y               | z               |
|--------|-------------|-----------------|-----------------|
| Sn     | 1.401422972 | 0               | 1.24958438      |
| Mo     | -1.467965496| 2.64368161      | 1.37461835      |
| O1     | 2.393844724 | 3.533405043     | -3.237345244    |
| O2     | 0.53075447  | 4.013502969     | -2.271782778    |
### β-SnWO₄

|       | x          | y          | z          |
|-------|------------|------------|------------|
| Sn    | -9.94778367 | -9.94778367 | -9.94778367 |
| W     | 1.144352421 | 1.144352421 | 1.144352421 |
| O1    | 2.160309292 | 2.160309292 | 2.160309292 |
| O2    | -0.866551666 | -1.57667516 | -3.162159637 |

### α-SnMo₀.₂₅W₀.₇₅O₄ (Space Group P2 No. 3)

|       | x          | y          | z          |
|-------|------------|------------|------------|
| Sn1   | 1.411365044 | -0.009461718 | 1.24622833  |
| Sn2   | -1.360922495 | -0.004969603 | -1.266770514 |
| Mo    | -1.544603227 | 2.646528994 | 1.374374678 |
| W1    | -1.354785467 | -2.64540869 | 1.369274251 |
| W2    | 1.422532454  | -2.646528994 | -1.374374678 |
| W3    | 1.322900756  | 2.64540869  | -1.369274251 |
| O1    | 2.38997326   | 3.450917162 | -0.254887181 |
| O2    | 0.378531185  | -3.600737606 | -0.349725814 |
| O3    | -2.405211745 | -3.596060307 | 0.361257395 |
| O4    | -0.417989479 | 3.489510134  | 0.263175051 |
| O5    | 0.582391448  | 4.095624961  | -2.189278308 |
| O6    | 2.271195233  | -3.951000604 | -2.298527845 |
| O7    | -0.513777004 | -3.958881849 | 2.31085694  |
| O8    | -2.258577704 | 4.124576785  | 2.249662953 |

### β-SnMo₀.₂₅W₀.₇₅O₄ (Space Group R3 No. 146)

|       | x          | y          | z          |
|-------|------------|------------|------------|
| Sn1   | -0.950701635 | -0.950701635 | -0.950701635 |
| Sn2   | -2.674891234 | 0.986164022  | 2.455227668 |
| Mo    | 1.015864361  | 1.015864361  | 1.015864361  |
| W     | 2.628494829  | -1.230997013 | -2.456429128 |
| O1    | 2.05621497   | 2.05621497   | 2.05621497   |
| O2    | 1.279582582  | -2.127117118 | -1.792725186 |
| O3    | -1.092577021 | -1.138212141 | -3.12420392 | 0.416285712 |
| O4    | -2.663018489 | 2.098537984  | 3.053572356  |
| O5    | 3.000420645  | -2.019540755 | 3.053572356  |
| O6    | 0.760667603  | 1.991388647  | -0.467481067 |

### α-SnMo₀.₅₀W₀.₅₀O₄ (Space Group P22₁2 No. 17)

|       | x          | y          | z          |
|-------|------------|------------|------------|
| Sn    | 1.338186162 | 0.009252515 | 1.26578916 |
| W     | -1.375429976 | 2.645332992 | 1.368851448 |
| Mo    | -1.237179005 | -2.645332992 | 1.368851448 |
| O1    | 2.441041861 | 3.676570963  | -0.392266662 |
| O2    | 0.421084163  | -3.357954437 | -0.1608942 |
| O3    | 0.522106459  | 3.876660645  | -2.341445597 |
| O4    | 2.165628879  | -4.225329353 | -2.14349098 |
\[ \beta-\text{SnMo}_{0.50}\text{W}_{0.50}\text{O}_{4} \text{ (Space Group P2, No. 4)} \]

|      | x               | y               | z               |
|------|-----------------|-----------------|-----------------|
| Sn1  | -1.040638566    | -0.974515755    | -1.058865785    |
| Sn2  | -2.515860562    | 1.034590838     | 2.540351673     |
| W    | 1.195007168     | 1.15083618      | 1.207337642     |
| Mo   | 2.380383106     | -1.132976283    | -2.40416327     |
| O1   | 2.175474534     | 2.200632052     | 2.225504476     |
| O2   | 1.320012454     | -2.148126698    | -1.363793047    |
| O3   | -1.033083779    | -1.630816178    | -3.203200221    |
| O4   | -2.73558359     | 1.503108322     | 0.364812804     |
| O5   | -3.220862121    | -0.889472224    | -1.5757918      |
| O6   | -1.545721475    | -3.173391761    | -0.818995549    |
| O7   | -0.363636868    | 0.892909935     | 1.954520669     |
| O8   | -1.940039958    | 3.166155571     | 2.530034037     |

\[ \alpha-\text{SnMo}_{0.75}\text{W}_{0.25}\text{O}_{4} \text{ (Space Group P2 No. 3)} \]

|      | x               | y               | z               |
|------|-----------------|-----------------|-----------------|
| Sn1  | 1.386729148     | -0.010721913    | 1.20380533      |
| Sn2  | -1.330216009    | -0.00878396     | -1.21152826     |
| Mo1  | -1.614766612    | 2.762084144     | 1.297267933     |
| Mo2  | -1.175014293    | -2.771375438    | 1.311857381     |
| Mo3  | 1.594217314     | -2.762084144    | -1.297267933    |
| W    | 1.134732961     | 2.771375438     | -1.311857381    |
| O1   | 2.232479433     | 3.387116357     | -0.150300004    |
| O2   | 0.440156075     | -3.573061264    | -0.170341686    |
| O3   | -2.324678318    | -3.564920828    | 0.178825789     |
| O4   | -0.463682114    | 3.408608424     | 0.067514862     |
| O5   | 0.596509996     | 4.410801671     | -2.080114067    |
| O18  | 2.23983         | -4.28006        | -2.15527        |
| O7   | -0.543048409    | -4.312568553    | 2.159898062     |
| O8   | -2.203667539    | 4.351360195     | 2.060498127     |

\[ \beta-\text{SnMo}_{0.25}\text{W}_{0.75}\text{O}_{4} \text{ (Space Group R3 No. 146)} \]

|      | x               | y               | z               |
|------|-----------------|-----------------|-----------------|
| Sn1  | -1.004450214    | -0.947113391    | -1.034619067    |
| Sn2  | 0.979198018     | 2.551218615     | -2.551218615    |
| Mo   | 1.130818696     | 1.105603568     | 1.156514061     |
| W    | -1.144259042    | -2.386157591    | 2.386157591     |
| O1   | 2.148353118     | 2.161625595     | 2.199494574     |
| O2   | -2.160725042    | -1.369691591    | 1.369691591     |
| O3   | -0.988925574    | -1.567663444    | -3.170712153    |
| O4   | -2.662270561    | 1.542019658     | 0.360138525     |
| O5   | 2.772095823     | -2.073808399    | 3.177807262     |
| O6   | 0.88662755      | 2.001566818     | -0.369208109    |
Table S4. Elongation (λ) and angular variance (σ) distortion parameters of MoO₄ and WO₄ tetrahedra in the β and α phases.

|        | β-SnMoO₄ | β-SnWO₄ | α-SnMoO₄ | α-SnWO₄ |
|--------|----------|----------|----------|----------|
| λ      | 1.0015   | 1.0001   | 1.047    | 1.028    |
| Σ      | 6.14     | 0.36     | 186.54   | 103.81   |

**Figure S1**: Variation with temperature of the Gibbs energy of β-SnWO₄ with respect to α-SnWO₄.

**Figure S2**: β and α structures highlighting the lone electron pair regions (yellow) associated with the SnO₃E and SnO₄E units. Sn-O bonds within these units are depicted as green-red bicolor cylinders, whereas the remaining Sn-O bonds of the SnO₆ (β-phase) and SnO₈ (α-phase) polyhedral are shown as dashed black lines. Blue transition metal polyhedral are highlighted. Green, and red balls stand for Sn and O atoms, respectively.
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