Electronic Supplementary Material (ESI) for RSC Advances.


# Structural and Electronic Properties of the $PbCrO_4$ Chrome Yellow Pigment and of Its Light Sensitive Sulfate-Substituted Compounds

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## SUPPORTING INFORMATION

**Table S1.** Cell parameters of the experimental and optimized cell structures of m-$PbCrO_4$, o-$PbCrO_4$ and the o-$PbSO_4$.

| | Experimental | | | Optimized | | |
|---|---|---|---|---|---|---|
| | **m-PbCrO4** | **o--PbCrO4** | **o-PbSO4** | **m-PbCrO4** | **o--PbCrO4** | **o-PbSO4** |
| **a (Å)** | 7.120 | 8.799 | 6.958 | 7.104 | 8.195 | 7.124 |
| **b (Å)** | 7.430 | 5.734 | 8.480 | 7.427 | 5.705 | 8.632 |
| **c (Å)** | 6.790 | 7.274 | 5.398 | 6.762 | 7.478 | 5.530 |
| **alpha (deg.)** | 90 | 90 | 90 | 89.9 | 90 | 90 |
| **beta (deg.)** | 102.4 | 90 | 90 | 102.5 | 90 | 90 |
| **gamma (deg.)** | 90 | 90 | 90 | 90.1 | 90 | 90 |
| **Volume ($Å^3$)** | 350.796 | 366.997 | 318.486 | 348.423 | 349.589 | 317.337 |

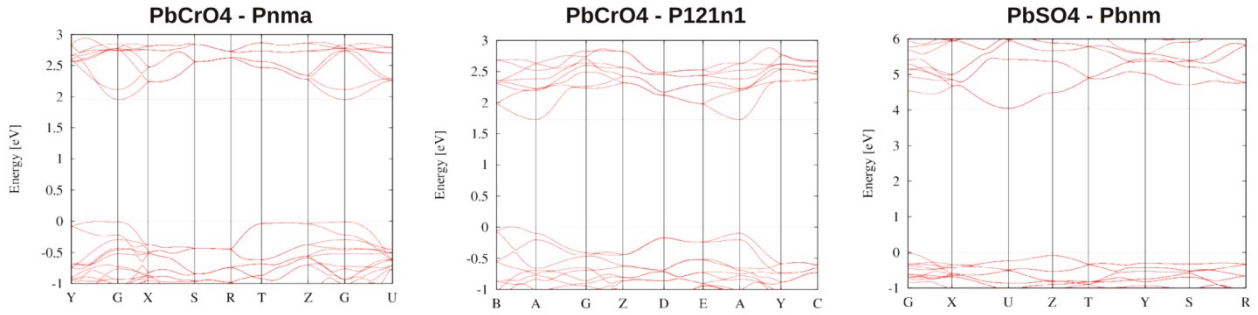


**Figure S1.** Band structures computed by SR-DFT on the experimental cell structures of m-$PbCrO_4$, o-$PbCrO_4$ and the o-$PbSO_4$. The zero has been set to the top of the valence band.

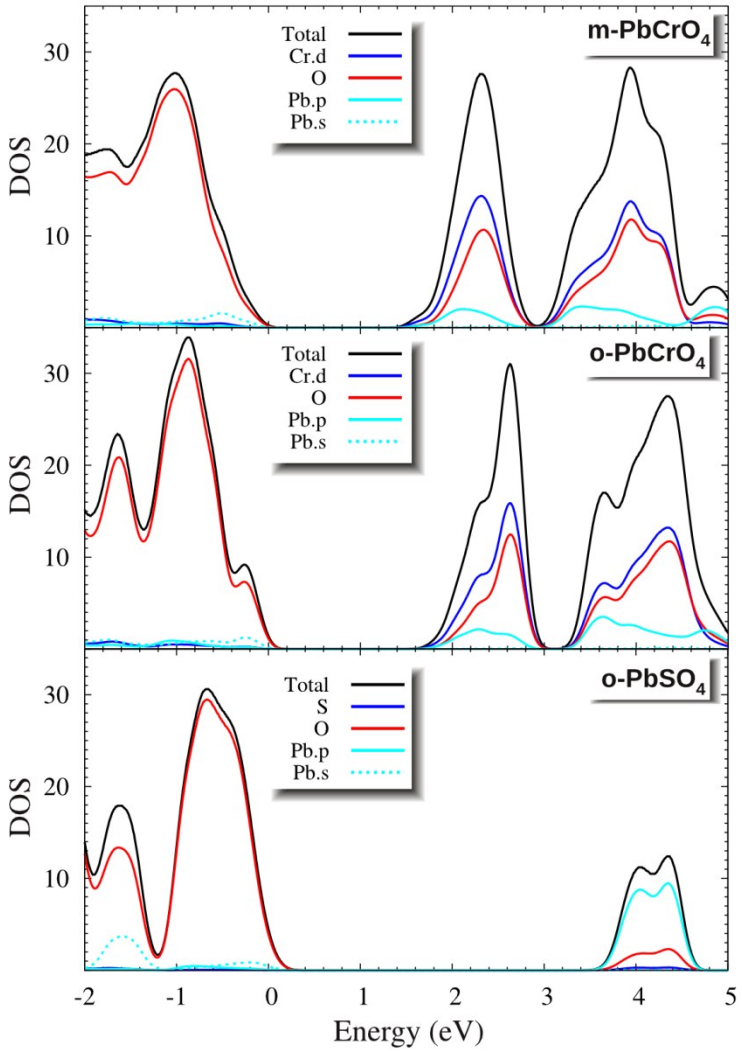


**Figure S2.** Total density of states for m-PbCrO4 (top), o-PbCrO4 (middle) and the o-PbSO4 (bottom) structures at the experimental cell parameters. Contribution of the main orbitals to the valence and conduction bands. The DOS have been aligned using the Pb.d peaks (spin down) and the zero has been set to the top of the m-PbCrO4 valence band.

**Table S2.** Relative stabilities (kcal/mol of the mixed $PbCr_{0.5}S_{0.5}O_4$ species with respect to the stablest one within the monoclinic or orthorhombic phase

| | **$PbCr_{0.5}S_{0.5}O_4$ (a** | **$PbCr_{0.5}S_{0.5}O_4$ (b** | **$PbCr_{0.5}S_{0.5}O_4$ (c** |
|---|---|---|---|
| **Monolclinic** | 0.68 | 0.02 | 0.00 |
| **Orthorombic** | 0.81 | 1.13 | 0.00 |

**Table S3.** High conduncion band conposition for the monoclinic species.

**x=0 x=0.25 x=0.5(c) x=0.75 x=1**

| | | | | | |
|---|---|---|---|---|---|
| Int. Limits | **3.01** | **3.00** | **3.03** | **3.06** | **3.16** |
| (eV) | **5.97** | **5.75** | **5.58** | **5.35** | **5.06** |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **45** | **36** | **31** | **22** | |
| Cr.p | | | | | |
| OCr.p | **35** | **31** | **26** | **18** | |
| OCr.s | **5** | **5** | **3** | **3** | |
| OS.p | | | **3** | **5** | **11** |
| OS.s | | | **2** | **3** | **8** |
| Pb.d | | | | | |
| Pb.p | **11** | **23** | **31** | **44** | **75** |
| Pb.s | **1** | **1** | **1** | **1** | |
| S.p | | | **1** | **1** | **3** |
| S.s | | | | | **1** |

**Table S4.** Low conduncion band conposition for the monoclinic species.

| | **x=0** | **x=0.25** | **x=0.5(c)** | **x=0.75** | **x=1** |
|---|---|---|---|---|---|
| Int. Limits | **1.27** | **1.27** | **1.38** | **1.41** | |
| (eV) | **3.01** | **3.01** | **3.03** | **3.06** | |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **52** | **52** | **51** | **51** | |
| Cr.p | | | | | |
| OCr.p | **36** | **36** | **35** | **34** | |
| OCr.s | **1** | **1** | **1** | | |
| OS.p | | | **1** | **2** | |
| OS.s | | | | | |
| Pb.d | | | | | |
| Pb.p | **8** | **8** | **8** | **9** | |
| Pb.s | | | | | |
| S.p | | | | | |
| S.s | | | | | |

**Table S5.** High valence band conposition for the monoclinic species.

| | **x=0** | **x=0.25** | **x=0.5(c)** | **x=0.75** | **x=1** |
|---|---|---|---|---|---|
| Int. Limits | **-1.45** | **-1.39** | **-1.34** | **-1.35** | **-1.26** |
| (eV) | **0.40** | **0.41** | **0.48** | **0.51** | **1.06** |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **2** | **2** | **1** | **1** | |
| Cr.p | | | | | |
| OCr.p | **89** | **84** | **42** | **19** | |
| OCr.s | **1** | **1** | | | |
| OS.p | | **6** | **49** | **72** | **93** |
| OS.s | | | | | |
| Pb.d | | | | | |
| Pb.p | **2** | **2** | **2** | **2** | **2** |
| Pb.s | **5** | **5** | **5** | **5** | **4** |
| S.p | | | | | |
| S.s | | | | | |

**Table S6.** Low valence band conposition for the monoclinic species.

| | x=0 | x=0.25 | x=0.5(c) | x=0.75 | x=1 |
|---|---|---|---|---|---|
| Int. Limits | **-5.27** | **-5.14** | **-4.92** | **-4.75** | **-4.30** |
| (eV) | **-1.45** | **-1.39** | **-1.34** | **-1.35** | **-1.26** |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **16** | **17** | **13** | **7** | |
| Cr.p | | | | | |
| OCr.p | **75** | **69** | **45** | **26** | |
| OCr.s | **2** | **2** | **1** | **1** | |
| OS.p | | **3** | **31** | **54** | **86** |
| OS.s | | | | **1** | **1** |
| Pb.d | | | | | |
| Pb.p | **3** | **4** | **4** | **4** | **4** |
| Pb.s | **3** | **2** | **3** | **4** | **4** |
| S.p | | | **1** | **1** | **1** |
| S.s | | | | | |

**Table S7.** High conduncion band conposition for the orthorombic species.

| | x=0 | x=0.25 | x=0.5(c) | x=0.75 | x=1 |
|---|---|---|---|---|---|
| Int. Limits | **3.44** | **3.28** | **3.14** | **3.17** | |
| (eV) | **6.04** | **5.38** | **5.24** | **5.23** | |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **44** | **21** | **21** | **22** | |
| Cr.p | | | | | |
| OCr.p | **34** | **18** | **18** | **18** | |
| OCr.s | **5** | **2** | **2** | **2** | |
| OS.p | | **4** | **4** | **5** | |
| OS.s | | **2** | **2** | **3** | |
| Pb.d | | | | | |
| Pb.p | **13** | **44** | **44** | **45** | |
| Pb.s | **1** | | | | |
| S.p | | | | **1** | |
| S.s | | | | | |

**Table S8.** Low conduncion band conposition for the orthorombic species.

| | x=0 | x=0.25 | x=0.5(c) | x=0.75 | x=1 |
|---|---|---|---|---|---|
| Int. Limits | **1.67** | **2.08** | **1.94** | **1.53** | **2.69** |
| (eV) | **3.09** | **3.28** | **3.14** | **3.17** | **4.59** |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **51** | **51** | **51** | **51** | |
| Cr.p | | | | | |
| OCr.p | **36** | **33** | **33** | **33** | |
| OCr.s | **1** | | | | |
| OS.p | | **2** | **2** | **2** | **11** |
| OS.s | | | | | **8** |
| Pb.d | | | | | |
| Pb.p | **9** | **10** | **10** | **10** | **75** |
| Pb.s | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| S.p | | | | | **3** |
| S.s | | | | | **1** |

**Table S9.** Low valence band conposition for the orthorombic species.

| | **x=0** | **x=0.25** | **x=0.5(c)** | **x=0.75** | **x=1** |
|---|---|---|---|---|---|
| Int. Limits | **-0.26** | **-1.11** | **-1.25** | **-1.26** | **-1.73** |
| (eV) | **0.64** | **0.78** | **0.64** | **0.63** | **0.59** |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **4** | | | | |
| Cr.p | | | | | |
| OCr.p | **74** | **21** | **21** | **21** | |
| OCr.s | **1** | | | | |
| OS.p | | **72** | **72** | **72** | **93** |
| OS.s | | | | | |
| Pb.d | | | | | |
| Pb.p | **2** | **1** | **1** | **1** | **2** |
| Pb.s | **17** | **3** | **3** | **3** | **4** |
| S.p | | | | | |
| S.s | | | | | |

**Table S10.** High valence band conposition for the orthorombic species.

| | **x=0** | **x=0.25** | **x=0.5(c)** | **x=0.75** | **x=1** |
|---|---|---|---|---|---|
| Int. Limits | **-5.46** | **-4.42** | **-4.56** | **-4.61** | **-4.77** |
| (eV) | **-0.26** | **-1.11** | **-1.25** | **-1.26** | **-1.73** |
| Cr.1s | | | | | |
| Cr.2s | | | | | |
| Cr.d | **16** | **7** | **7** | **7** | |
| Cr.p | | | | | |
| OCr.p | **75** | **25** | **25** | **25** | |
| OCr.s | **2** | **1** | **1** | **1** | |
| OS.p | | **54** | **54** | **54** | **86** |
| OS.s | | **1** | **1** | **1** | **1** |
| Pb.d | | | | | |
| Pb.p | **3** | **4** | **4** | **4** | **4** |
| Pb.s | **2** | **4** | **4** | **4** | **4** |
| S.p | | **1** | **1** | **1** | **1** |
| S.s | | | | | |

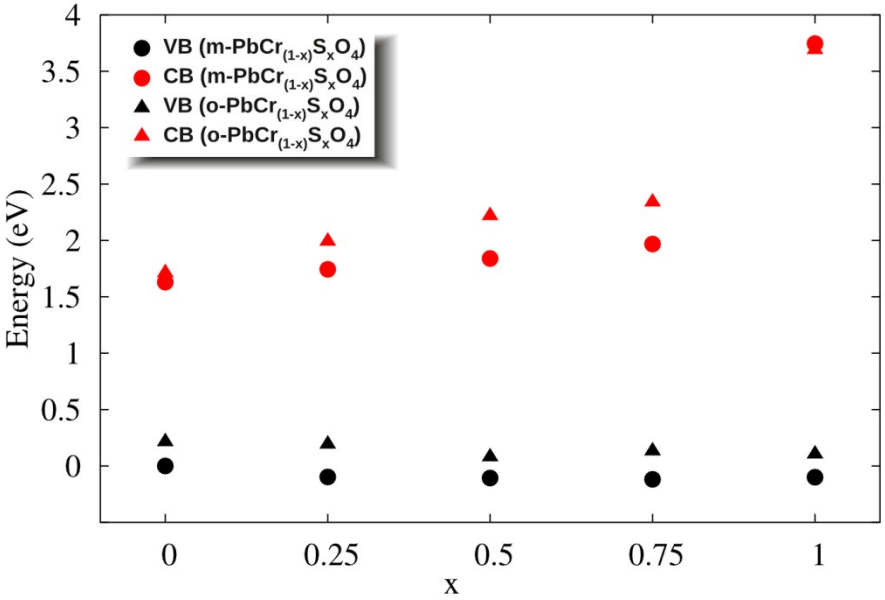


**Figure S3.** Valence and conduction band for the monoclinic and orthorhombic mixed species.

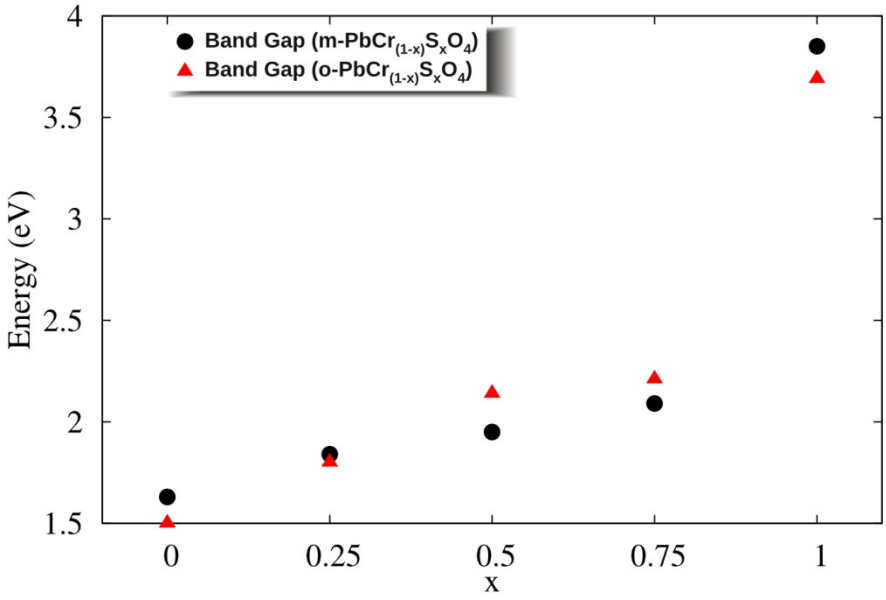


**Figure S4.** Band gap for the monoclinic and orthorhombic mixed species

**Table S11.** Average distances (Å), volumes (Å$^3$) and effective coordination numbers for the $CrO_4^{2-}$ and $SO_4^{2-}$ tetrahedra and the $PbO_9$ polyhedra for the monoclinic structures.

| | | x=0 | x=0.25 | x=0.5 (a) | x=0.75 |
|---|---|---|---|---|---|
| $CrO_4^{2-}$ | **CrO dist. (Å)** | 1.654 | 1.654 | 1.654 | 1.654 |
| | **Pol volume (Å$^3$)** | 2.315 | 2.314 | 2.309 | 2.311 |
| | **Coord. Number** | 3.997 | 3.997 | 3.998 | 3.998 |
| $SO_4^{2-}$ | **SO dist. (Å)** | - | 1.493 | 1.494 | 1.493 |
| | **Pol volume (Å$^3$)** | - | 1.705 | 1.707 | 1.703 |

| | | | | | |
|---|---|---|---|---|---|
| | **Coord. Number** | - | 3.993 | 3.996 | 3.995 |
| **$PbO_9$** | **PbO dist. (Å)** | 2.675 | 2.677 | 2.679 | 2.685 |
| | **Pol volume (Å$^3$)** | 37.404 | 37.505 | 37.632 | 37.909 |
| | **Coord. Number** | 7.562 | 7.709 | 7.949 | 8.104 |
| | **Val. Band (eV)** | 0.00 | -0.10 | -0.11 | -0.12 |
| | **Cond. Band (eV)** | 1.63 | 1.74 | 1.84 | 1.97 |
| | **B-gap (eV)** | 1.63 | 1.84 | 1.98 | 2.09 |

**Table S12** Average distances (Å), volumes (Å$^3$) and effective coordination numbers for the $CrO_4^{2-}$ and $SO_4^{2-}$ tetrahedra and the $PbO_x$ polyhedra for the orthorhombic structures.

| | | **x=0** | **x=0.25** | **x=0.5 (a)** | **x=0.75** |
|---|---|---|---|---|---|
| **$CrO_4^{2-}$** | **CrO dist. (Å)** | 1.653 | 1.652 | 1.651 | 1.650 |
| | **Pol volume (Å$^3$)** | 2.315 | 2.311 | 2.308 | 2.303 |
| | **Coord. Number** | 3.984 | 3.985 | 3.989 | 3.987 |
| **$SO_4^{2-}$** | **SO dist. (Å)** | - | 1.492 | 1.492 | 1.492 |
| | **Pol volume (Å$^3$)** | - | 1.704 | 1.701 | 1.702 |
| | **Coord. Number** | - | 3.993 | 3.978 | 3.989 |
| **$PbO_9$** | **PbO dist. (Å)** | 2.541 | 2.707 | 2.802 | 2.788 |
| | **Pol volume (Å$^3$)** | 19.102 | 29.564 | 42.860 | 42.456 |
| | **Coord. Number** | 5.688 | 5.896 | 6.179 | 7.183 |
| | **Val. Band (eV)** | 0.21 | 0.19 | 0.08 | 0.13 |
| | **Cond. Band (eV)** | 1.71 | 1.99 | 2.22 | 2.34 |
| | **B-gap (eV)** | 1.50 | 1.80 | 2.14 | 2.21 |