Supplementary information

A Layered Wide-Gap Oxyhalide Semiconductor with an Infinite ZnO$_2$ Square Planar Sheet: Sr$_2$ZnO$_2$Cl$_2$

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Figure S1. Rietveld structural refinement against the synchrotron diffraction patterns collected from \( \text{Sr}_2\text{ZnO}_2\text{Cl}_2 \) at room temperature. The zinc oxychloride adopts the \( \text{I}_4/\text{mmm} \) space group with \( a = 4.06981 \) Å and \( c = 15.20076(8) \) Å. Sr on 4e (0, 0, 0.39328(5)), Zn on 2a (0, 0, 0), O on 4c (0, 0.5, 0) and Cl on 4e (0, 0, 0.18260(1)). No deficiencies were found at all site occupancies. Isotropic atomic displacement parameters (\( B_{\text{iso}} \)) were 0.252(2) Å\(^2\) for Sr, 0.25(2) Å\(^2\) for Zn, 0.8(1) Å\(^2\) for O and 0.28(5) Å\(^2\) for Cl. Reliability factors were \( R_{wp} = 1.154\% \) and \( R_B = 1.451\% \).
Figure S2. Rietveld structural refinement against the neutron diffraction patterns collected from Sr$_2$ZnO$_2$Cl$_2$ at 3 K. The zinc oxychloride adopts the $I4/mmm$ space group with $a = 4.057723(1)$ Å and $c = 15.114116(4)$ Å. Sr on 4e (0, 0, 0.39208(8)), Zn on 2a (0, 0, 0), O on 4c (0, 0.5, 0), and Cl on 4e (0, 0, 0.18225(7)). The site occupancy factors ($g$) were fixed at those obtained from the refinements using the 300 K data, namely, $g$(Zn) = 0.962 and $g$(Cl) = 0.950. Isotropic atomic displacement parameters ($B_{iso}$) were 0.204(3) Å$^2$ for Sr, 0.03(5) Å$^2$ for Zn, 0.408(1) Å$^2$ for O, and 0.2150(4) Å$^2$ for Cl. Reliability factors were $R_{wp} = 8.88\%$ and $R_B = 3.83\%$, and Goodness-of-fit = 1.8.
Figure S3. Temperature evolution of the lattice constants, volume, Zn–O/Zn–Cl bond lengths, and Sr–O/Sr–Cl bond lengths, which were obtained by Rietveld structure refinements.
Figure S4. Laboratory X-ray diffraction (Cu-Kα radiation) patterns collected from Ba$_2$ZnO$_2$Cl$_2$ at room temperature, which was synthesized at 1800 °C and 6 GPa. Due to the hygroscopic nature, the powder sample was suspended in liquid paraffin for the measurement. The XRD data were readily assigned by the $I4/mmm$ space group with $a = 4.2570(2)$ Å and $c = 15.969(1)$ Å. In the XRD patterns, wurtzite ZnO and unidentified peaks were detected as impurities. Vertical lines represent expected Bragg peak positions for Ba$_2$ZnO$_2$Cl$_2$ ($I4/mmm$) and wurtzite ZnO.
Figure 5. Band dispersions for $\text{Sr}_2\text{ZnO}_2\text{Cl}_2$ calculated along high symmetry lines within the GGA framework.
Figure S6. Crystal Orbital Hamiltonian Population (COHP) for Zn-O interaction in Sr$_2$ZnO$_2$Cl$_2$. The COHP curve shows bonding state between Zn 3$d$ and O 2$p$ orbitals in the energy range from -8 to -6 eV, but antibonding states in the valence band maximum.