Supplementary information

A Layered Wide-Gap Oxyhalide Semiconductor with an Infinite ZnO_2 Square Planar Sheet: $Sr_2ZnO_2Cl_2$

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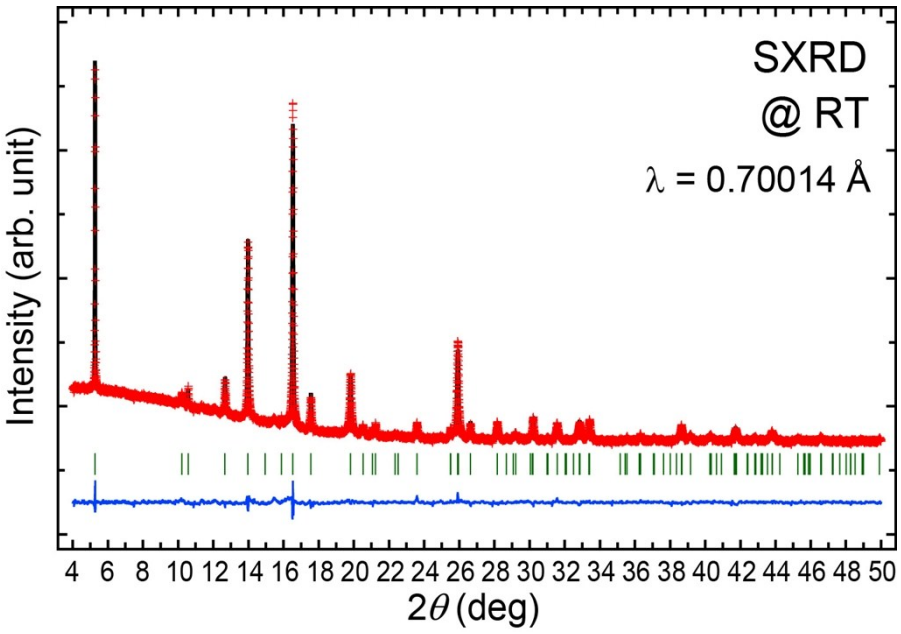

Figure S1. Rietveld structural refinement against the synchrotron diffraction patterns collected from $Sr_2ZnO_2Cl_2$ at room temperature. The zinc oxychloride adopts the *I*4/*mmm* space group with a = 4.06981 (2) Å and c = 15.20076(8) Å. Sr on 4*e* (0, 0, 0.39328(5)), Zn on 2*a* (0, 0, 0), O on 4*c* (0, 0.5, 0) and Cl on 4*e* (0, 0, 0.18260(1)). No deficiencies were found at all site occupancies. Isotropic atomic displacement parameters (B_{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%.

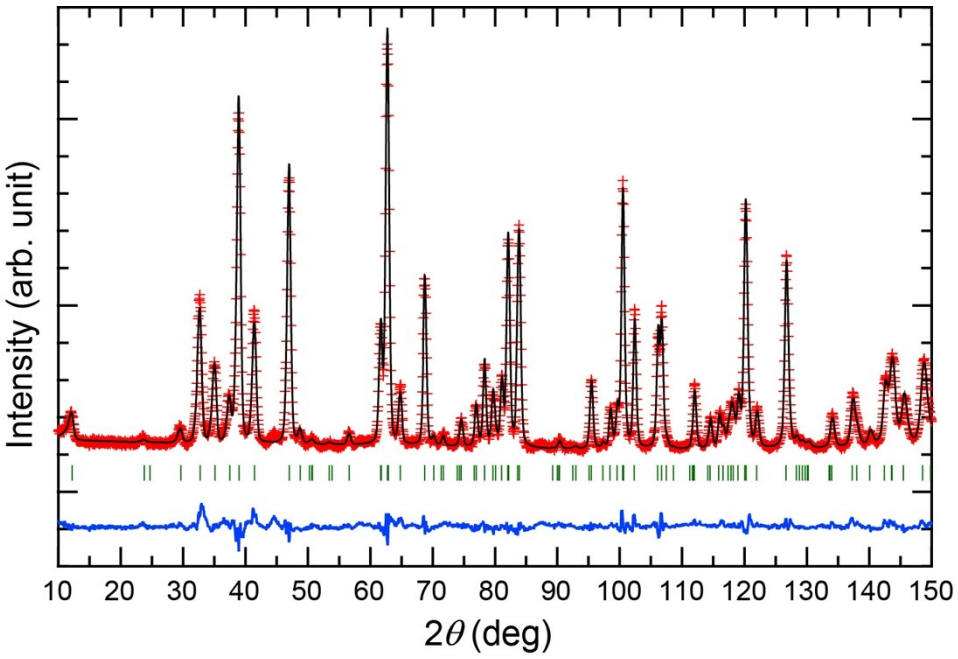

Figure S2. Rietveld structural refinement against the neutron diffraction patterns collected from $Sr_2ZnO_2Cl_2$ at 3 K. The zinc oxychloride adopts the *I*4/*mmm* space group with a = 4.057723(1) Å and c = 15.114116(4) Å. Sr on 4*e* (0, 0, 0.39208(8)), Zn on 2*a* (0, 0, 0), O on 4*c* (0, 0.5, 0), and Cl on 4*e* (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.

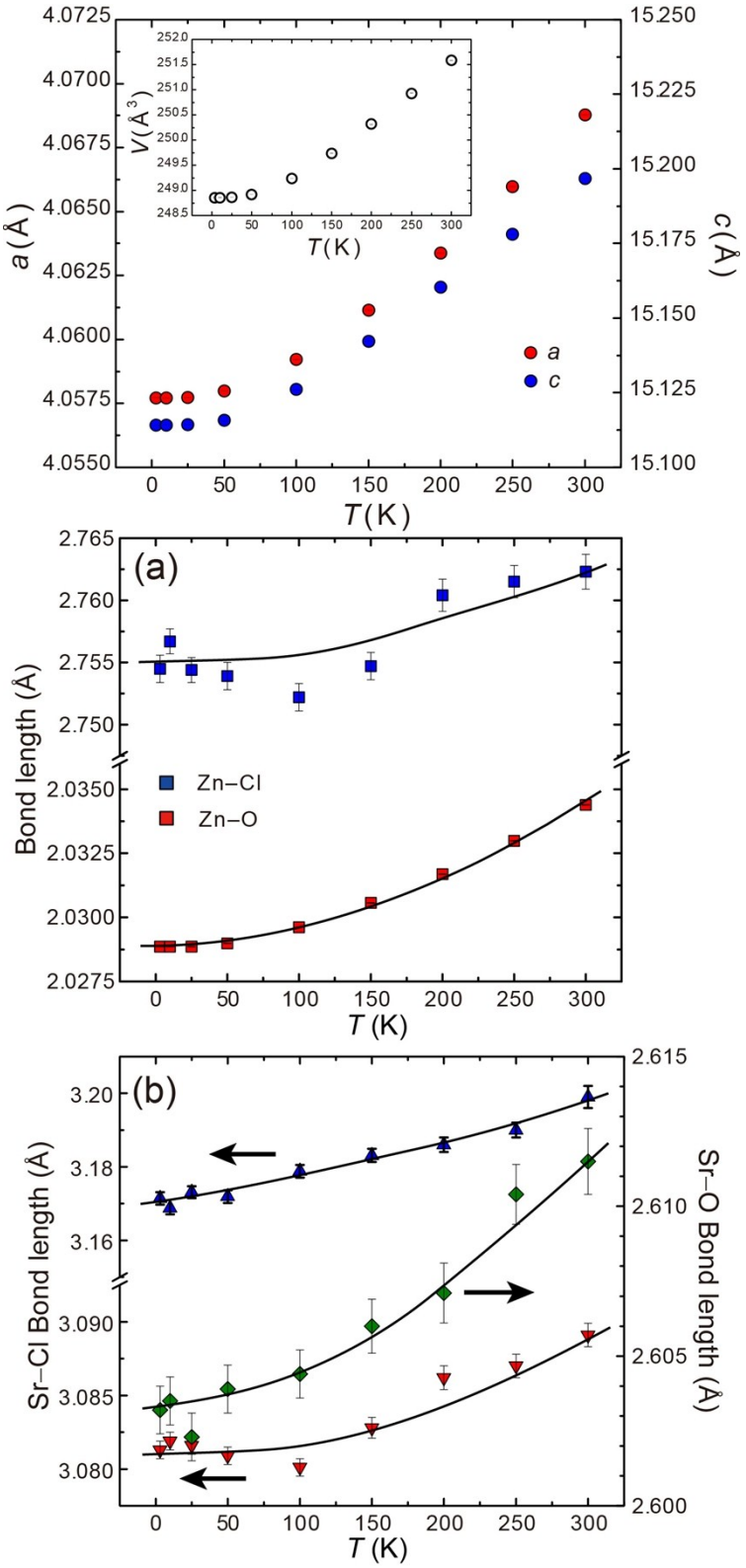

Figure S3. Temperature evolution of the lattice constants, volume, Zn–O/Zn–Cl bond lengths, and Sr–O/Sr–Cl bond lengths, which were obtained by Rietveld structure refinements.

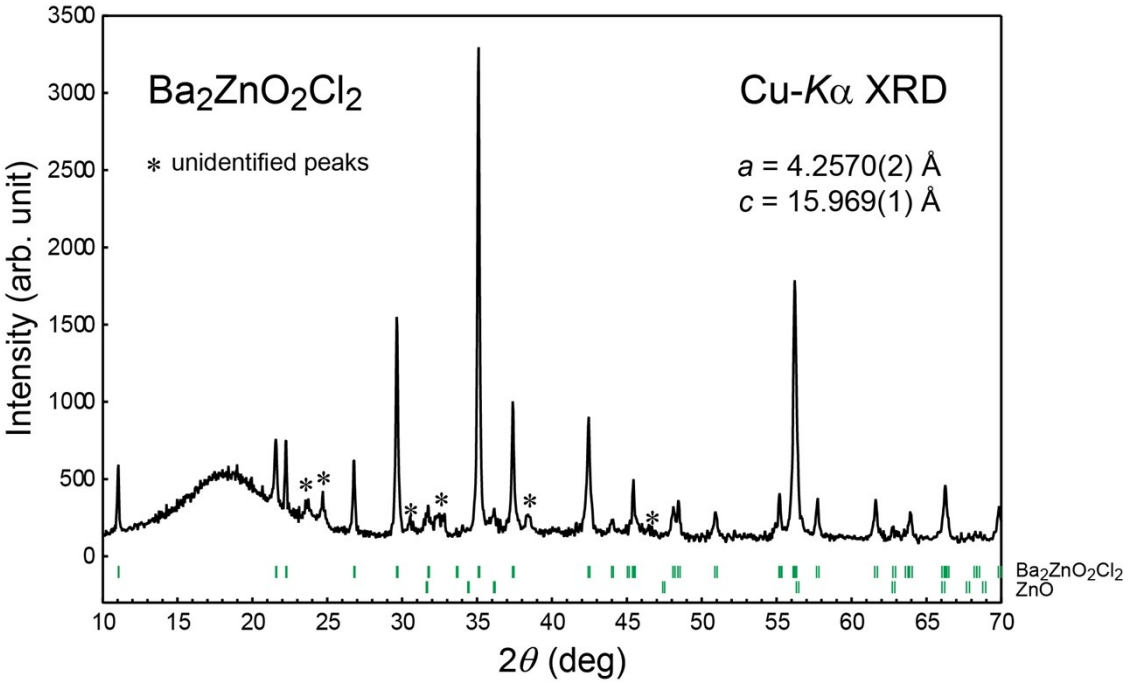

Figure S4. Laboratory X-ray diffraction (Cu-K_α radiation) patterns collected from $Ba_2ZnO_2Cl_2$ at room temperature, which was synthesized at 1800 °C and 6 GPa. Due to the hygroscopic nature, the powder sample was suspended in liquid paraffin for the measurement. The XRD data were readily assigned by the *I*4/*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 $Ba_2ZnO_2Cl_2$ (*I*4/*mmm*) and wurtzite ZnO.

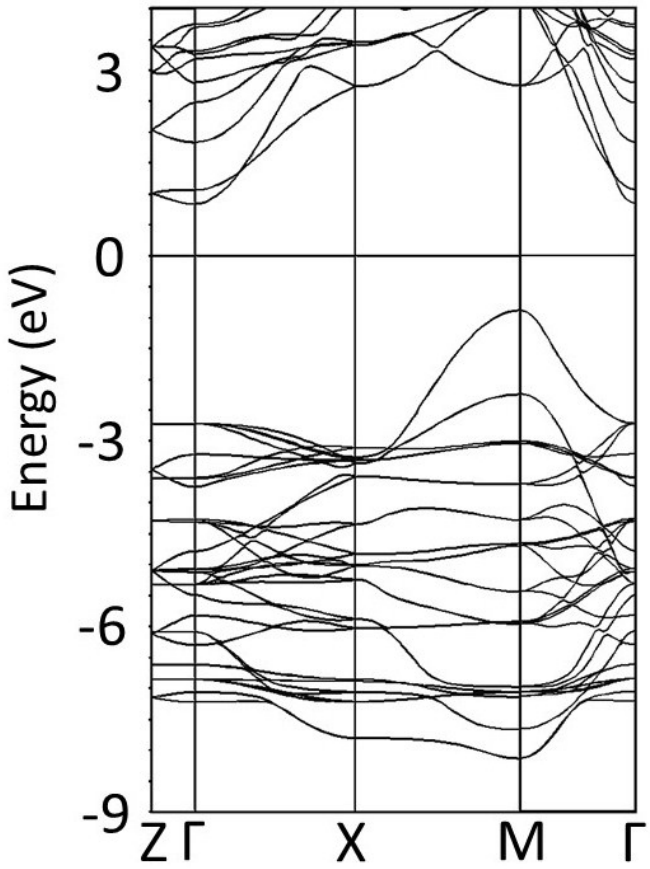

Figure 5. Band dispersions for $Sr_2ZnO_2Cl_2$ calculated along high symmetry lines within the GGA framework.

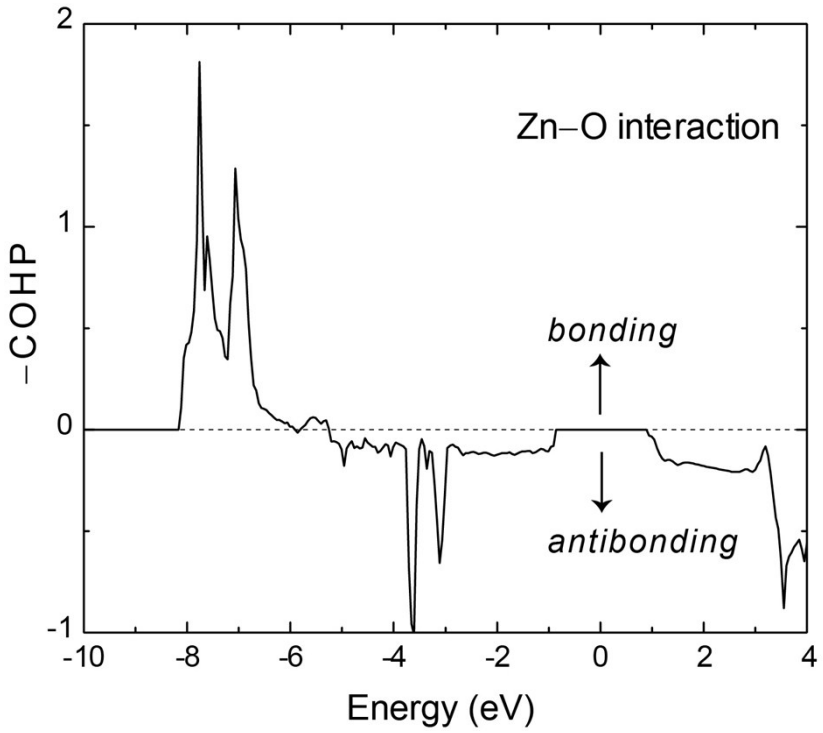

Figure S6. Crystal Orbital Hamiltonian Population (COHP) for Zn-O interaction in $Sr_2ZnO_2Cl_2$. The COHP curve shows bonding state between Zn 3*d* and O 2*p* orbitals in the energy range from -8 to -6 eV, but antibonding states in the valence band maximum.