

Crystal Structure, Electron Density and Covalent Bonding of a Visible Light Responsive Photocatalyst $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$

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Introduction

Metal oxysulfides have the potential to photocatalyze various reactions under visible light. For example, promising results have been reported for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, which has been demonstrated to be responsive to excitation at wavelengths up to ca. 650 nm, with a suitable band-gap position for overall water splitting. In the present work, the crystal structure and electron density of an active $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$ photocatalyst sample under visible-light excitation are investigated by synchrotron powder diffraction for high-precision analysis of the crystal structure and electron density. Density functional theory (DFT) is employed for theoretical calculations of the electron density distribution and partial density of states (PDOS). (M. Yashima, K. Ogisu and K. Domen, *Acta Crystallogr. B*, **64**, [3] 291-298 (2008)).

Experiments

Synchrotron x-ray powder diffraction experiments of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$ were performed at 299 K using the multiple-detector system installed at the BL-4B₂ beam line of the Photon Factory, KEK, Japan. A monochromatized 1.20643 Å x-ray beam was utilized. The crystal structure of the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$ was refined by the Rietveld method with a computer program RIETAN-2000 (Izumi & Ikeda, 2000). Electron-density distribution of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$ was investigated by a maximum-entropy method (MEM, PRIMA (Izumi & Dilanian, 2002)) and DFT calculations.

Results and discussion

The bond valence sums at the $\text{Sm}(\text{S}_5\text{O}_{14})$, $\text{Ti}(\text{O}_{14}\text{O}_2)$, $\text{S}(\text{Sm}_5\text{Ti}_1)$, $\text{O}1(\text{Sm}_2\text{Ti}_2)$, and $\text{O}2(\text{Ti}_2)$ coordinations were estimated to be 3.5, 3.9, 2.3, 2.0, and 2.1, consistent with the valences of Sm^{3+} , Ti^{4+} , S^{2-} , O^{2-} , and O^{2-} ions, respectively. Electron-density analysis based on synchrotron diffraction data in combination with DFT calculations clearly showed covalent bonding between Ti and O atoms and ionic bonding at the Sm–S, Sm–O and Ti–S bonds (Fig. 1). The results demonstrate that $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$ consists of two-dimensional networks of Ti–O1 covalent bonds. The overlap of O 2p and Ti 3d orbitals is responsible for the covalent bonds between Ti and O atoms, and the presence of S 3p orbital and the

overlap of the O 2p and Ti 3d orbitals result in enhanced dispersion of the valence band, raising the top of the valence band and realizing visible-light response. The S 3p and Ti 3d orbitals and covalent Ti–O bonds are thus expected to be responsible for the small band-gap energy exhibited by $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$, allowing photocatalysis to occur at visible wavelengths of as long as 650 nm. The S 3p and Ti 3d orbitals and covalent Ti–O bonds may thus be a fundamental basis for the design of Ti-based oxysulfide photocatalysts with activity under visible light.

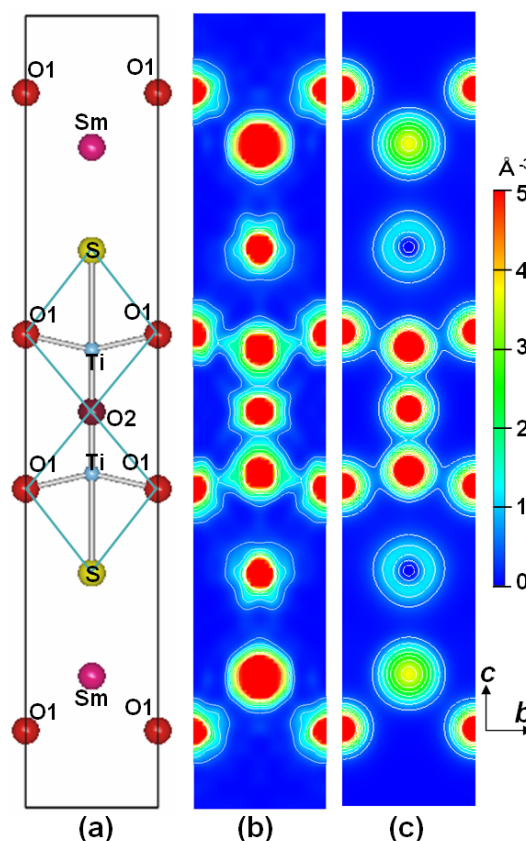


Fig.1. (a) Refined crystal structure and (b) MEM electron-density distribution on the b - c plane of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_{4.9}$. (c) DFT valence electron-density distribution on the b - c plane of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ at $x = 1/2$. White contour lines: 0.5 to 5 \AA^{-3} in 0.5 \AA^{-3} steps.

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