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Title: High-Conductive Protonated Layered Oxides from H₂O Vapor-Annealed Brownmillerites

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Abstract: The uptake of hydrogen and oxygen ions in transition-metal oxides (TMOs) may lead to the discovery of triple ionic-electronic conducting materials. However, the currently employed redox approaches hindered the co-insertion of them. Thus, we introduced an acid-based thermal hydration method for the systematic discovering of high conductive protonated oxides from the oxygen-deficient TMOs. We illustrated our strategy by synthesizing a layered [Sr₂O₂H₂]_{0.5}CoO₂ oxyhydride from the brownmillerite SrCoO_{2.5} and explain the non-topotactic phase transition with a proton-triggered cation exchange mechanism mediated by the presence of oxygen vacancies. [Sr₂O₂H₂]_{0.5}CoO₂ unlocks an unprecedented triple ionic-electronic conduction down to 250 °C and a thermoelectric power up to 3.51 mW/K²m at room temperature from the insulating SrCoO_{2.5} parent phase. These findings open up opportunities for systematically preparing protonated multifunctional oxides.

One Sentence Summary: By thermal hydration SrCoO_{2.5} transforms into a layered SrCoO₃H, a material with superior proton conducting and thermoelectric properties.

Main Text:

Hydrogen and oxygen ions provide the most accessible and effective means of inducing phase transformations that elicit novel structures and properties in TMOs. Although the uptake of each individual ions has been intensely studied (1-11), the simultaneous co-insertion of them was scarcely reported. The was primarily due to the highly selective activation of the hydrogen or oxygen ions upon a specific redox stimulus. The currently employed methods, such as thermal annealing by O₂/O₃ (12, 13) or H₂/CO (14, 15), ionic liquid gating(2, 7), plasma implementation (6), chemical reaction with oxidants or metal-hydrides(8, 10, 16), and electrochemical redox reaction (3, 17) *etc.*, were oxidizing and reducing incompatible at the same time. Since these either-or redox approaches hindered the co-uptake of hydrogen and oxygen ions, an alternative strategy was the acid-based combination reaction that integrated both hydrogen and oxygen ions (*i.e.*, H₂O). In TMOs, the water uptake could be illustrated by $H_2O + V_O^{\bullet\bullet} + O_O^{\times} = 2OH_O^{\bullet}$, where the $V_O^{\bullet\bullet}$, O_O^{\times} and OH_O^{\bullet} represented the Oxygen vacancy, lattice O and hydroxyl, respectively (18, 19). Such a reaction was used to describe the exchange behavior at the surface regime of a catalyst operating in humid gas environment, where the water-driven phase transformations were deliberately avoided and thus adequately neglected. Although this non-redoximorphic H₂O uptake pointed out a realistic route for inserting hydrogen and oxygen ions simultaneously, the water-contained transport kinetics and water-integrating phase transformation has yet to be explored clearly. As one can expect, a successful resultant that uptakes H₂O directly leads to a hydrogen and oxygen ion conducting material, which is of significant interest for an emerging class of triple ionic-electronic conduction (TIEC) materials (19-24), if the electronic conduction could be enhanced at the meanwhile.

In this report, we introduced a scalable, high-yield and cost-efficient water-vapor annealing method to consistently discover high conductive protonated oxides from oxygen-deficient TMOs. We illustrated the efficiency and technical soundness of our method by synthesizing the novel layered oxyhydride [Sr₂O₂H₂]_{0.5}CoO₂ (SCOH) from the oxygen-deficient SrCoO_{2.5} (BM-SCO). As expected, the charge and pH neutral H₂O did not induce a reduction or oxidization, but only act as a dopant source. This thermal hydration approach generated high proton concentration layered compounds, and thus unlocked the TIEC and unexpected outstanding thermoelectric power from the insulating BM-SCO parent phases. The SrCoO_{2.5} was selected because the Co-based TMOs were widely used in water-involved catalysis (22, 24-28) on the one hand; on the other hand, its structure linked to several prosperous families of materials such as perovskite (29), Ruddlesden-Popper (30, 31), 2H-perovskite (32, 33) and misfit-layered compounds (34-37) that exhibit intriguing physical and chemical properties.

Fig. 1A illustrates schematically the thermal hydration on BM-SCO thin films. BM-SCO is a reduced form of the perovskite SrCoO_{3.6} that is characterized by columns of ordered $V_O^{\bullet\bullet}$ along its pseudo-tetragonal [110] direction (9, 17), which offers an X-ray detectable structure feature for the oxygen evolution. Interestingly, a new phase (SCOH) formed from BM-SCO upon water vapor treatment as shown by the XRD θ - 2θ scans of Fig. 1B for thin films annealed in 1 bar O₂ and 1bar O₂+H₂O atmospheres. Except for the *c*-lattice constant, which slightly decreased from 3.97 Å to 3.96 Å, little change was observed for dry O₂ annealing. However, the BM-SCO disappeared when the sample was exposed to wet O₂ and a new SCOH phase emerged with a significantly increased *c* lattice parameter (9.06 Å). The thickness of the corresponding film

approximately was 19 nm and only minor changes were observed after annealing (fig S1). The transformation from BM-SCO to SCOH did not depend on the gas species (O₂ or air), only on the water vapor (fig. S2). The transformation was not affected by the epitaxial strain introduced by the substrate, at least for (La,Sr)(Al,Ta)O₃ (LSAT) and SrTiO₃ (STO) (fig. S3). The new SCOH structure resulted from a non-topotactic phase transition (38-40) since the corresponding diffraction peaks did not follow those of the starting BM-SCO phase and the O₂ concentration barely impacted the transformation.

XRD and High-resolution Scanning Transmission Electron Microscopy (HR-STEM) were employed to identify the SCOH structure. Fig. 1C shows the in-plane wide area reciprocal space mapping (WARSM) of the SCOH thin film. A triclinic geometry with $a=b=7.48$ Å (fig. S4), $\gamma=84^\circ$ and its 90° rotation counterpart (fig. S5) was first identified (T-SCO). Although all these diffractions can be indexed by T-SCO, the T (3 $\bar{1}$ 0) and T (1 $\bar{3}$ 0) exhibit 10 times higher intensity than their counterparts. That means they overlap with other diffractions (green labeled). These spots belong to a hexagonal-like geometry H-SCO) with $a=2.90$ Å, $b=2.82$ Å and $\gamma=120^\circ$ (fig. S6). The epitaxial directions are LSAT [110] and [$\bar{1}$ 10]. The skew angles α and β are determined to be 90° and 95.5° by the fast Fourier transformation (FFT) of (220) and (2 $\bar{2}$ 0) plane, respectively (fig. S7). The lattice constants are summarized in table S1. Figs. 1D-I present the High-Angle Annular Dark Field (HADDF)-STEM images of SCOH (220) and (200) planes as well as the corresponding Energy Disperse X-ray Spectroscopy (EDS) mapping and Annular Bright Field (ABF) images. SCOH consists of a bright Co-based layer and two dark Sr-based layers. The stacking of Sr layers is very much like those of rock-salt sheets in Ruddlesden-Popper Sr₂CoO₄ (30). The Co layers are unresolvable in the (200) plane due to its zone axis is 12° off the Sr layer. For the (220) plane, the ABF image shows that the skewed Co-O cage is the same as the edge-sharing Co-O octahedra in the CdI₂ type. Thus, the T-SCO layer is Sr₂O₂, while the H-SCO layer is CoO₂. The strain between the SCOH thin film and the substrate is relaxed by the stacking fault at the interface, see fig. S8.

With this information, the SCOH skeleton is proposed as $[\text{Sr}_2\text{O}_2]_{2.90 \times 2.82 \times \sin 120^\circ} [\text{CoO}_2]_{3.74 \times 3.74 \times \sin 84^\circ}$, or $[\text{Sr}_2\text{O}_2]_{0.5}\text{CoO}_2$. Its atomic structure is shown in fig. S9, which belongs to the P2/m space symmetry group. Such an alternate stacking of layers with very differentiated geometries belongs to the so-called misfit-layered compounds (41). Owing to the alternation of transition-metal conducting and insulating rock-salt layers in the stacking sequence on the principle of high thermopower resulting from the first type of layers and low thermal conductivity from the second (42), $[\text{Sr}_2\text{O}_2]_{0.5}\text{CoO}_2$ unlocks the thermoelectricity from BM-SCO by thermal hydration.

Figs. 2A & B evidence H₂O uptake occurring during the BM-to-layered phase transition. The FT-IR absorbance near 3340 nm⁻¹ proves directly the existence of hydroxyl groups in SCOH. The second-ion mass spectroscopy (SIMS) depth profiles of the H₂O/D₂O/H₂¹⁸O vapor annealed thin films show that the intensity of H⁻/D⁻/¹⁸OH⁻ ions increase to thousands of counts within the film regime by annealing, and dropped to the pristine level after dehydration. The enrichment of ¹⁸O at the surface region reflects V_O^{••} accumulation and the ions distribution indicate a layer-by-layer conversion mode, and is verified in fig. S10. Therefore, we propose that the H₂O molecules, rather than H or O ions alone, insert into the thin film and trigger the phase transition. SCOH can then be alternatively described as SrCoO_{3- δ} (H₂O) _{δ} , where δ represents oxygen deficiency. A variety of techniques based on redox reactions have been proposed to introduce light elements like H and O in the BM-SCO V_O^{••} positions with the aim of enhancing functionality (1-3, 5, 7, 43). However, due to selective switching limitations H and O co-doping

cannot be efficiently achieved through redox-based methods. Here, through the water vapor annealing, we doped the oxygen-deficient perovskite with H₂O successfully.

Figs. 2C & D demonstrate the occurrence of H₂O decomposition within SCOH by temperature-dependent XRD and thermogravimetry-mass spectroscopy (TG-MS). Under a 1 bar air atmosphere (RH ~ 80%), the BM-SCO transformed to SCOH at approximately 250 °C. At 400 °C, the SCOH (003) peak shifted slightly to the left and finally skipped to 2θ=27° at 550 °C. According to TG-MS, the stepwise increases of *c*-lattice constant then resulted from a two-stage water decomposition process. The mass reduction of 0.4% at 400 °C (S₁) and 3.8% at 550 °C (S₂) correspond to H₂O decomposition of 0.044 and 0.401 mol/formula, respectively. The S₀ peak at 117 °C came from the surface water desorption. The small S₁ hump probably was originated from residual H ions hopping in the CoO₂ layers. The S₂ main peak, on the other hand, resulted from the majority of H ions in the Sr₂O₂ layers at equilibrium. It is worth noting that a broadened S₂ gap is observed for the Sr₂O₂ layers corresponding to the dehydrated SCOH (fig. S11), which explains the XRD peak skip at 550 °C.

Figs. 2E-H describe the changes in the electronic structure before and after the phase transformation. The XPS spectra in Figs. 2E & G exhibit little change for either the line shape or the peak-to-peak energy difference, which means that the cobalt ions chemical states are dominant and pretty close to Co³⁺. The line shape of O 2*p* is quite similar to that of Li_{0.94}CoO₂ (44). The XAS of O 1*s* in Fig. 2G, on the other hand, reflects rather different electronic configurations (fig. S12) between the two. In the octahedra crystal ligand field BM-SCO, the electronic configuration of the Co^{III} 3*d*-O 2*p* hybridized orbital corresponds to a high spin state *e_g²t_{2g}⁴* (3). In the triangular crystal field of SCOH, the small bump *α* that appears at low energies arises from an electronic transition from a O 2*p* state to the half-filled *a_{1g}* state of the hybridized orbital Co^{IV} 3*d*-O 2*p* in hydrogen deficient SCOH. Meanwhile, the pronounced feature *γ* originates from an electronic transition from a O 2*p* state to the empty *e_g* state of the hybridized orbital Co^{III} 3*d*-O 2*p* (45). Therefore, the electronic configuration of SCOH is primarily a null spin state *e_g⁰a_{1g}²e_g¹* mixed with a small portion of low spin state *e_g⁰a_{1g}¹e_g¹*. The content of H can be estimated from the intensity ratio *γ*/(*α*+*γ*), which here amounts to 0.95. Thus, the SCOH thin film is actually SrCoO₃H_{0.95}, which agrees with the results from the TG-MS analysis. Both the XPS and XAS spectra prove that there is little change in the chemical state of the Co ions after water vapor annealing, thus supporting the non-redox nature of the H₂O uptake reaction. Both these results confirm also that the number of H in stoichiometry SCOH is fairly close to 1. Thus, the total reaction can be written as SrCoO_{3-δ} (s) + δH₂O (g) = [Sr₂O₂H_{2δ}]_{0.5}CoO₂ (s) (0.25 ≤ δ ≤ 0.5).

It is noted that the number of inserted H₂O molecules equals the number of V_O^{••}. Such an equivocal correspondence can be used to accurately gauge the concentration of oxygen vacancies in nonstoichiometric oxides, *n_v*, which represents an important long standing technical challenge. Conventionally, *n_v* is roughly estimated through XRD, XAS or magnetization (9, 38, 46), whereas here it can be accessed directly by evaluating the concentration of H ions. Practically, the proton concentration is able to be controlled in the resulted materials by the number of oxygen vacancies in the perovskites parent phase. Here, by annealing SrCoO_{2.5} in water vapor, we obtained the SCOH whose proton concentration is far from the defect level. The protons in the layered transition-metal oxides are readily movable at the temperature as low as 250 °C, and non-volatile for temperature as high as 550 °C. These features make [Sr₂O₂H₂]_{0.5}CoO₂ a potential candidate for being a proton-conducting oxide (20).

The H₂O decomposition shown in Fig. 2D and [fig. S11](#) indicates a tendency for the protons to stay in the Sr₂O₂ layers. However, direct observation of the H positions is a very difficult and arduous task as demonstrated by the simulation of the corresponding STEM geometry output ([fig. S13](#)). First-principles calculations based on density functional theory (DFT) were undertaken to determine the most likely H sites in the Sr₂O₂ layers. The results are shown in Fig. 3G & H. According to our DFT calculations, the H ions prefer to form hydroxyls with the O atoms in the Sr₂O₂ rather than CoO₂ layers as the later leads to a CoOOH-like structure (27) which would attain extra *c*-lattice expansion. The hydroxyls point to the adjacent CoO₂ layers and form energetically favorable hydrogen bonds with the closest oxygen, which explains the appearance of small OH⁻ tilting along the [110] direction and the *a*-axis elongation of the H-SCO layers. With the H insertion, the symmetry of SCOH reduced to space group P1.

The atomistic mechanism involved in the non-topotactic protonation of BM-SCO during the thermal hydration is proposed to consist of several cations' exchanges mediated by V_O^{••}, as represented in Fig. 3. First, a H₂O molecule is captured and dissociated into a OH⁻ and a H⁺ by a metal cation (M), namely, H₂O + MO_O[×] = HO-M-O_O[×]H (47), or by an oxygen vacancy following H₂O + V_O^{••} + O_O[×] = 2OH_O[•] (19) (Fig.3A). At elevated temperatures, the protons are able to hop to the inner Sr-O layers and form hydroxyl bonds (Fig. 3B). Each hydroxyl bond unlocks a Sr ion from the Sr-O layer (Fig. 3C), which diffuses to a V_O^{••} position in the Co-O tetrahedra layer along the [111] direction (Fig. 3 D), thus forming a Sr vacancy (V_{Sr}^{''}). Subsequently, a Co ion diffuses to V_{Sr}^{''} (Fig. 3E) so that the Sr and Co cations exchange their sites through a V_O^{••}. Then two layers of Co ions and 3 layers of O ions transform to one CdI₂-type CoO₂ layer. Meanwhile, the dangling O from H₂O inserts to the as-formed surface V_O^{••} (Fig. 3 F). Both the proton and oxygen ions from the H₂O molecule are thus incorporated into the newly formed [Sr₂O₂H₂]_{0.5}CoO₂ lattice. During this process the proton moves in the opposite direction than V_O^{••}, thus the net charge flow along the *c*-axis is null. As the reaction proceeds, the inner BM-SCO layers repeat phase transformation steps A - F in Fig. 3 using the O ions and protons transported by the top SCOH layer. By means of DFT methods, we estimated the total energy of the system during each phase transformation step ([fig. S14](#)). Our DFT results show that the BM-SCO to [Sr₂O₂H₂]_{0.5}CoO₂ reaction mechanism is overall downhill made the exception of step 3 => 4 in which the Sr ions diffuse towards the V_O^{••} positions. This partial outcome was physically expected as Sr possesses the largest ionic radius.

From the previous analysis, it is shown that the presence of V_O^{••} is a necessary condition for the water vapor-driven phase transformation to proceed. Further tests were undertaken to prove this point. For instance, we treated the SCO perovskite under a 1 bar O₂ + H₂O atmosphere and observed that the thin film was completely transformed to SCOH ([fig. S15](#)). This occurred because in a low oxygen concentration atmosphere the perovskite SCO was appropriately reduced to BM-SCO (1). However, when the BM-SCO thin film was annealed in a 10 bar O₂ + H₂O atmosphere, only a part of the thin film transformed to SCOH ([fig. S16](#)) due to the fact that in a high oxygen concentration atmosphere the V_O^{••} in BM-SCO are occupied by O atoms (13).

Fig. 4 shows the characterization of BM-SCO before and after thermal hydration. The temperature dependent resistivity in Fig. 4A demonstrates that the SCOH thin film is semi-metallic between 2 and 300 K. The conductivity increases in at least 4 orders of magnitude as compared to that of the parent BM-SCO. This high electronic conductivity plus the ability of

transporting O ions and protons boosts $[\text{Sr}_2\text{O}_2\text{H}_2]_{0.5}\text{CoO}_2$ an excellent candidate for triple ionic-electronic conducting oxides for next-generation electrochemical devices (21). Fig. 4B shows the experimental Seebeck coefficient (S) of BM-SCO and SCOH over the temperature interval 400 - 10 K. The S positive sign implies that both BM-SCO and SCOH are p -type conductors. Although the conductivity increases significantly, the S coefficient of SCOH only decreases slightly. Fig. 4C shows that at 300 K the power factor of SCOH is about 2250 times than that of BM-SCO, thus demonstrating a marked increase in the electrical conductivity while retaining excellent thermoelectric power. At room temperature, the power factor of SCOH attains the value 3.51 $\text{mW/K}^2\text{m}$, which approximately is 15 times larger than that of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films (48), superior than that of ZnO (49) and comparable to that of state-of-the-art Bi_2Te_3 (table S2), which shows that layered $[\text{Sr}_2\text{O}_2\text{H}_2]_{0.5}\text{CoO}_2$ is an outstanding thermoelectric oxide material (50-53). The optical transmittance in Fig. 4D shows that the transparency of the SCOH thin film stabilizes at 80% in the infrared light range and improves up to 20% in the visible light range than that of the BM-SCO. The absorption edge shifts to the violet side, and the optical band gap is estimated to be 2.61 eV which is 0.33 eV wider than the BM-SCO. Combined with the thermoelectricity, the transparent semi-metallic SCOH thin film exhibits great potential for hybrid energy harvesting such as transparent conductive window and thermoelectric solar cells.

The inverse magnetic susceptibility (χ) of SCOH is shown in Fig. 4E as a function of temperature. Between 2 and 400 K, the measured data is well described by the Curie-Weiss law using the $\chi = \chi_0 + C/(T - \theta)$, where χ_0 is a temperature independent contribution. The Curie constant C is fitted to be 0.023. Using the $C \approx n(n+2)/8$ (54), the unpaired electrons n is calculated to be 0.09 ($S \approx 0$), which well agrees with the XAS results. From our spin-polarized DFT calculations, it was found that for the lowest-energy state the Co electrons arrange over the d orbitals according to a low-spin (LS) state characterized by null Co magnetic moments (Fig. 4F). In particular, the energy of the Co LS state was estimated to be 45 meV per formula unit below that of the corresponding Co high-spin (HS) state (for both possible ferromagnetic and antiferromagnetic spin structures). This theoretical outcome is in consistent agreement with our experimental measurements. We note that the impact of the selected U parameter value on our DFT results was carefully investigated (fig. S17). Therefore, based on our experiments and DFT calculations we can conclude that SCOH is a nonmagnetic semi-metal.

In summary, we employed the water vapor to anneal the oxygen-deficient $\text{SrCoO}_{2.5}$ thin film and thus synthesized a novel layered-oxyhydride $[\text{Sr}_2\text{O}_2\text{H}_2]_{0.5}\text{CoO}_2$, which exhibited triple ionic-electronic conduction, thermoelectricity, optical transparency and nonmagnetic semi-metal that unprecedented in the parent phase. We demonstrated that the uptake of water into the thin film drove the bulk-to-layered phase transformation, and proposed a proton-triggered cation exchange mechanism mediated by the presence of oxygen vacancies to explain the unravelled non-topotactic phase transition. The resulted material is a good candidate for electrodes of low-temperature thermoelectric PCFCs, thermoelectric solar cells or transparent conductive window that boosts synergistic energy harvesting (55). Our work shows the great potential of hydrogen and oxygen co-doping in reconstructing TMOs for advanced energy conversion, and the use of thin film as a clean platform to study the ions exchange and transport in TMOs. Such an acid-based ions insertions override the selective switching in redox reaction, which is sufficiently general to allow the prediction of a new class of proton-containing multifunctional oxide materials from brownmillerites such as $\text{CaFeO}_{2.5}$, $\text{CaCoO}_{2.5}$, $\text{GaInO}_{2.5}$ etc., or any oxygen-deficient oxides such as WO_x , VO_x , TiO_x , BaCoO_{3-6} , SrNiO_{3-6} . Alternatively, the ions co-doping reminds a revisit to the TMOs cathode materials for possible enhancement or degradation of

performances due to the water-induced phase transformation. Future work, for example, the measurement of individual hydrogen and oxygen ionic conductivity upon different atmospheres or the anisotropy ions diffusion, are highly preferred to further understand the ions transfer in TMOs.

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Supplementary Materials:

Materials and Methods

Figures S1-S18

Tables S1-S2

References (57-79)

Fig. 1. Preparation and structure characterization of SCOH thin films. (A) A schematic view of thermal hydration on SCO thin films. (B) XRD θ - 2θ scans of as-grown BM, 1bar O₂ annealed and 1bar O₂ + H₂O annealed SCO thin films grown on LSAT substrate. (C) In-plane WARSM of SCOH thin film. The q coordinates have been divided by LSAT d_{100} . The white grids corresponding to the integers h , k are guides to eyes. The spots of rotated H-SCO are marked by hexagons. (D) & (G) HADDF-STEM, (E) & (H) EDS mapping and (F) & (I) ABF images for the SCOH (220) & (200) plane, respectively. The Sr, Co and O atoms are painted by red, green and blue, respectively.

Fig. 2. H₂O evolution during the BM-to-layered phase transition. (A) FT-IR spectroscopy of BM-SCO and SCOH powder. (B) SIMS depth profiles of H₂O, D₂O and H₂¹⁸O vapor annealed SCO thin films. The pristine BM-SCO and dehydrated SCOH were used for comparison. The film/substrate interface is marked by green. (C) XRD peak evolution of BM-SCO thin film by heating the sample in wet atmosphere. (D) TG-MS investigation on SCOH powder. (E) X-ray photoelectron spectroscopy (XPS) of Co 2*p*, (F) O 1*s*, (G) X-ray absorption spectroscopy (XAS) of Co *L*-edge and (H) O *K*-edge of BM-SCO and SCOH thin films.

Fig. 3. Water vapor-driven brownmillerite-to-layered phase transformation in strontium cobaltite thin films illustrated by 7 quasi-stable intermediate states. (A) H₂O absorption and dissociation on the surface BM-SCO. (B) Protons hop to the O sites in Sr-O layer. (C) The formation of hydroxyl unlocks Sr from the Sr-O matrix. (D) Sr atoms diffuse to the oxygen vacancies in tetrahedra Co-O layer. (E) Co atoms diffuse to the previous Sr vacancies in Sr-O layer. In consequence, the Sr and Co atoms exchange their sites between layers. (F) Two Co layers and their neighboring O atoms transform to the CdI₂-type Co-O octahedra. Meanwhile, the O from H₂O intercalates into the oxygen vacancy in the surface Sr-O layer. (G) The (110) and (H) (100) planes of the resulted SrCoO₃H.

Fig. 4. Properties of SCO thin films before and after thermal hydration. (A) Temperature dependent resistivity, (B) Seebeck coefficient, (C) thermoelectric power factor, (D) optical transmittance, (E) inversed magnetic susceptibility vs. temperature of BM-SCO and SCOH. (F) Total and partial Co *d* densities of electronic states calculated with DFT methods for bulk SCOH. Spin up and spin down densities of electronic states are represented along the positive and negative sections of the ordinate axis, respectively. Results were obtained for the ground-state null-spin solution found in the spin-polarised DFT calculations by using the range-separated hybrid HSE06 functional (56).