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Bandgap engineering of $Gd_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ double perovskite for photocatalysis applications

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ABSTRACT

To design the material rationally, we predict the effect of oxygen vacancy on the material bandgap and electron state density based on the first principle density functional theory. Crystal structure, electronic properties, as well as the oxidation and reduction states of $Gd_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ oxides were studied by GGA-PBE + U calculation. By changing one oxygen atom in the Gd-$O_{0.5}$ plane of supercell, $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.25}$ and $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.75}$ were created. And they show half-metallic and metallic properties respectively, which is related to the strong electronic correlations for 3d orbitals of Co. Calculation results of partial density of states suggest that O-2p and Co-3d orbits have a great effect on the band gap of $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.5}$, and the location of cobalt may be an active site. Besides, $Gd_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ were prepared and annealed in atmosphere to regulate the oxygen vacancy content. Hence, a deep and systematic study on $Gd_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ was conducted based on theoretical calculations and experiments, including crystal structure, electron distribution and oxygen vacancy. Differing from the conventional doping modification to adjust the electronic energy band structure, this work is dedicated to synthesizing the stable and efficient materials from the theoretical design, which providing a new feasible thought for the efficient and stable material design.

1. Introduction

Perovskite-type oxides are important inorganic functional materials. They have the general formula ABO_3, where A represents an alkaline earth metal and B is occupied by the transition metal. In this crystal structure, A sites have a large ionic radius cation coordinated to 12 oxygen atoms while B sites are occupied by a smaller one coordinated to 6 oxygen [1]. Perovskite oxides are tolerant to symmetry lowering lattice distortion and have the ability to tolerate a large number of defects, which makes it widely used in optical, electrical, biological and photocatalytic materials [2]. Especially, photoactivity of perovskite has been widely reported recently, such as titanate perovskites, tantalite perovskites and ferrite perovskites [3–7]. Tanaka and coworkers have concluded the advantages of perovskite photocatalysis as follows: 1) similar and basic structures; 2) well characterized structures and surface properties; 3) variable valences, stoichiometry and vacancies [8]. $A_2B_2O_6$, the general formula of double perovskites, is one of the complex perovskite-type oxides. Since the different cations at A or/and B sites, double perovskites have a general form $AA'BB'O_6$. Double perovskite is well known for highly efficient photocatalytic performance, such as Sr_2FeNbO_6, La_2FeTiO_6, Ba_2CoWO_6 and $Na_2Ta_2O_6$ [9–11]. The properties of double perovskites are closely related to the material compositions and chemical states, which involve the mixed valences and oxygen vacancies. Since the ambient environment can influence the formation of oxygen vacancies and then change the valences of variable elements, much work has been focused on the atmosphere heat treatment to improve performance so far [12–16].

The oxide $Gd_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ (GCBC), a known double perovskite oxides $GdBaCo_2O_{5+\delta}$ (GBCO), possesses interesting properties such as insulator-metal transition (IMT), magnetic transition and total conductivity [17,18]. These novel properties are closely bound up with the unusual structure. GCBC has $[GaO_\delta]$–$[CoO_2]$–$[BaO]$–$[CoO_2]$ square-lattice layer ordered along the c axis [19]. Moreover, the valence states of cobalt ions may change along with δ, and each state would have multifarious spin states further [20]. Thus, both the mixed valences of cobalt ions and oxygen vacancies are responsible for the electrical and optical properties of the materials. In addition, the infrared emissivity and optical properties of GCBC have been profoundly investigated in recent years [21,22]. However, studies on the photocatalytic activities of GCBC fabricated by systematic atmospheric treatment have been

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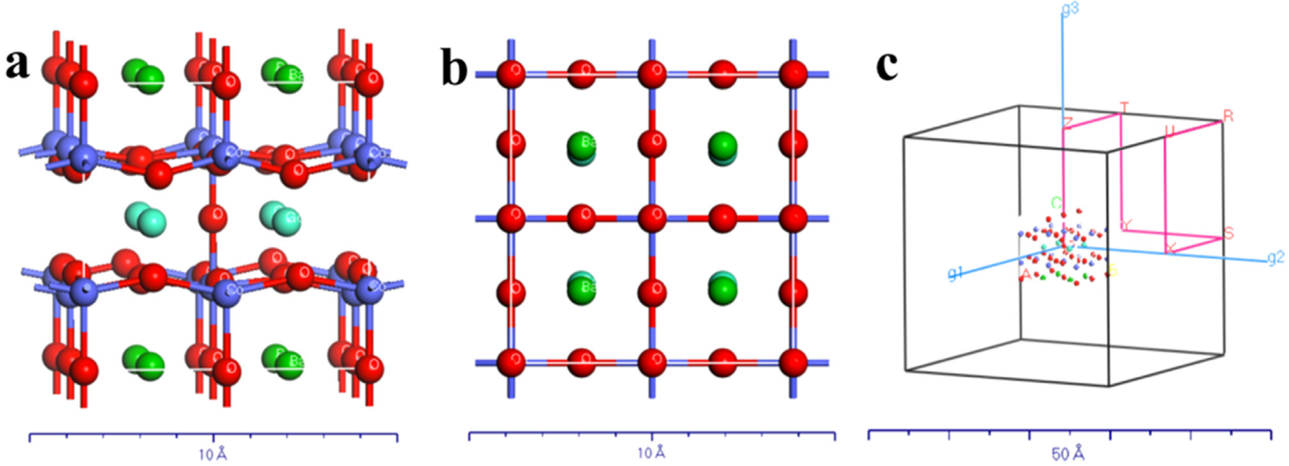

Fig. 1. Crystal structure of $GdBaCo_2O_{5+\delta}$ (a) and along [0 0 1] direction (b), primary Brillouin zone in reciprocal space and its k-lines (c).

rarely reported, especially combining it with theoretical simulation to systematically analyze catalytic mechanism.

In the present work, detailed first-principles computations were performed to investigate the basic characteristics of materials from microscopic scale, especially the band structure and densities of states of GCBC. What is more, GCBC was synthesized through sol-gel method and then annealed in oxygen atmosphere at different temperatures. We explored the influence of heat treatment temperature on the phase, composition, microstructure and photocatalytic performance. Based on the theoretical calculation and experiment, the materials were studied deeply and systematically from the aspects of crystal structure, electron distribution and oxygen vacancy. The results suggest that the photocatalytic process appears to be affected by the surface compositions and chemical states of samples.

2. Density functional theory (DFT) calculations

We first built the structure of $GdBaCo_2O_{5+\delta}$, which belongs to a double perovskite with BaO-CoO_2-$GdO_{0.5}$-CoO_2 planes alternating along the z axis direction. There are oxygen vacancies ordered in the $GdO_{0.5}$ planes along the x direction, as shown in Fig. 1. There are two kinds of Co that are nonequivalent in this structure and they are in an octahedral and square pyramidal environment respectively. The Co ions in $GdBaCo_2O_{5+\delta}$ are all found in high spin state [23,24]. A 2 × 2 × 2 supercells containing 38-atom is used to conduct structural optimizations. The unit cells with Ca-doped are based on this supercell, by introducing the dopant ion to the corresponding site. To calculate the total energy, we integrated the wave functions in the Brillouin region, and these points were accomplished by summing up some special k-points. K-lines for band structure calculation were colored in pink as shown in Fig. 1(c).

In GCBC, the localized 3d electrons of Co are subject to strong correlations, which could lead to a splitting of the 3d band into two sub bands. To account for the strong effect of such electrostatic repulsion correctly, DFT + U (on-site Coulomb correlations) approach was applied to this system [25–27]. According to the relevant previous reports, the U value for both the d-orbitals of Co and the f-orbitals of Gd was set to 5.0 eV in the present work [28,29]. Fig. 2 shows the total DOS of GCBC employing Hubbard U correction and that without it. The fermi energy was set at 0 eV. The structure employing U correction is found to be half-metal with a bandgap of 0.56 eV, which is corresponding to the charge transfer between O 2p and Co 3d states (Fig. 4). Meanwhile, the other one displayed metallic property. It indicates that the Hubbard-U correction promoted the description of d and f electron localization in the strong correction system.

As can be seen from Table 1, the theoretical lattice parameters of GCBC are close to the experimental ones. The ionic radius of Ca (0.99 Å) is little larger than that of Gd (0.938 Å), which could lead to a slight deformation of the unit cell volume. In sum, the experimental results are in good consistent with the theoretical ones, which confirms the reasonability of the simulation. As shown in Fig. S1, Ca-doped has influence on the electronic distribution around Fermi level of the band structure, which is described as below (Fig. 4). According to the PDOS analysis, it can be ascribed to the division for the 3d orbit of Co, which would lead to the reduction of valence state to a lower one by the adjacent oxygen vacancy. The isosurface of electron cloud is known as density surface. As can be seen from Fig. S1(b) and (d), the electron cloud around Ca is sparsest, implying that the whole electron density of the system has changed.

The density of state patterns in Fig. 3 shows the effect of oxygen vacancy on the total density and the electronic band structure near the Fermi energy. Oxidation and reduction were simulated by changing one oxygen atom in the supercell, leading to a compound with the chemical formula $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.75}$ and $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.25}$ respectively. To obtain the most stable structure, Gd-O plane was selected to add or remove oxygen ion according to the relevant reports [28,30]. As shown in Fig. 3, $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.25}$ remains a half-metal, while $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.75}$ is metallic. The electron structure near the Fermi level has been changed and the new state density peaks appear in the valence bands, which may be closely related to the strong electronic correlations for 3d orbitals of Co. It can be considered that the vacancy weakens the chemical bond between Co and O and affects the hybrid bond.

For metals and narrow-gap semiconductors, the densities of states around the Fermi energy represent the reactivity of the atom. Therefore, further analysis of the total and partial densities of states of $Gd_{0.8}Ca_{0.2}BaCo_2O_{5.5}$ can help to explain the properties of crystals at the electronic structure level. As presented in Fig. 4, the energy structure can be divided into five regions (except for the inner electron compounds): 1) the lowest area is set near − 25 eV, which is employed by the s orbitals of Ba; 2) the second area, in − 22 ~ − 15 eV, mainly originates from the p orbitals of Gd and Ca as well as the s orbitals of O; 3) the third area is located around − 11 eV and occupies by the p orbitals of Ba; 4) the area from − 10 eV to the top of the VBM is mainly initiated by the f orbitals of Gd, the p orbitals of O and the d orbitals of Co; 5) the last area ranges from 0 to 6 eV, which contributes to the conduction band, originating from the f orbitals of Gd and the d orbitals of Co. It is noteworthy that there is strong hybridization between the p orbitals of O and d orbitals of Co in the range of − 10 ~ 0 eV, indicating a strong chemical bond between the two. According to the analysis above, the influence factors of GCBC band gap mainly come from the orbits of O-2p and Co-3d. Because the surface states near Fermi level are