



Evaluation of the band-gap of Ruddlesden–Popper tantalates



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ABSTRACT

Tantalum-oxide based compounds of the $K_2[Ln_{n-1}Ta_nO_{3n+1}]$ cation-deficient Ruddlesden–Popper series are promising compounds as water splitting photocatalysts for hydrogen production. In this work the role of the lanthanide ($Ln = La, Pr$ and Nd) in the $K_2LnTa_3O_{10}$ tantalate for the photocatalytic mechanism is studied. The question arises as to whether it can be considered only as a “spectator” or if it contributes to this mechanism. The band gaps for the aforementioned tantalates are studied and here we evaluate how the localized $Ln:4f$ states are positioned in the gap. This system is analyzed with electronic structure calculations using a linearized augmented plane wave method based on Density Functional Theory. It was found that two of the lanthanide atoms, Pr and Nd , contribute with $4f$ state in the gap, and these states act as ‘stepping stones’ for the electrons to jump to the conduction band. This can be useful in designing and tuning future materials for hydrogen production in the semiconductor-mediated photocatalytic process of water splitting.

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1. Introduction

Ruddlesden–Popper phases can be described as intergrowths of the perovskite and rock salt structures following the formula $(AO)[ABO_3]_n$ or $A_2[A'_{n-1}B_nO_{3n+1}]$ where A and A' refer to an alkali, alkaline earth or rare earth (Ln) and B refers to a transition metal. Due to its optical and semiconducting properties, many of these compounds have been used in heterogeneous catalysis [1]. They mediate in photochemical reactions to oxidize organic contaminants and/or reduce metal ion contaminants in water supplies.

In addition to these applications, several studies have focused in finding materials that can use sunlight efficiently to decompose water into oxygen and hydrogen. Some of them have used computational screening to find materials that can be suitable for water splitting, among other purposes [2–4]. Directly related to the photo-catalytic activity of this kind of compounds is the study of their electronic structure [5,6]. Studying it permits to know – and hopefully modify – the band gap value, the carrier transport characteristics, the catalytic activity and chemical stability. One

important challenge is to “tune” the absolute position of the valence and conduction band edges. This helps the compound to reduce hydrogen ions (H^+) and to oxidize water (OH^-), producing hydrogen (H_2) and oxygen, respectively.

Developing different methods of Hydrogen production can have important environmental applications. In this sense, the Ruddlesden–Popper phases based on Tantalum oxide compounds have received much attention as promising photocatalysts of water splitting for Hydrogen production [7–9]. This includes lanthanum-doped $NaTaO_3$ with NiO as a co-catalyst, which has one of the highest efficiencies found [10,11]. Tantalum-oxide based compounds, crystallizing in the perovskite structure and others with a related structure as those of the Ruddlesden–Popper series and Dion-Jacobson phases have been also experimentally investigated [12,13].

In this work, we considered the system $K_2Ln_{n-2}Ta_nO_{3n+1}$, $n = 3$, (Fig. 1). When these compounds interact with water, they split in layers along the rock salt atoms (Fig. 2). The resulting layered structure is just a few perovskite wide. This has been observed experimentally in the system considered [14,15] as well as with other similar systems [8,16,17].

Our aims is to analyze whether if the A' ($Ln = La, Pr$ and Nd) cations of the $K_2LnTa_3O_{10}$ system should be considered as simple “spectators” or if this crystallographic position could be occupied by atoms which contribute with states near to the Fermi level. In

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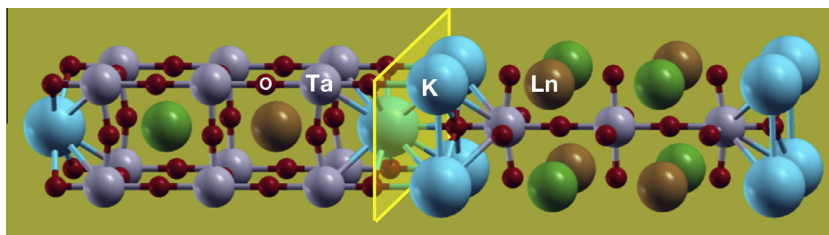


Fig. 1. Crystal structure of the cation deficient Ruddlesden–Popper tantalate $K_2LnTa_3O_{10}$. The figure shows the Potassium atoms in blue, the Lanthanide atoms in brown and green (only half are occupied), the Tantalum atoms in grey and the Oxygen atoms in red. In this work, we considered for the Lanthanide sites the following atoms: La, Nd and Pr. This system has a bidimensional repetition in the XY plane and it shows two planes of Potassium atoms, displaced between them. An imaginary plane dividing these two sections in the unit cell is shown in yellow. These Tantalum–oxide compounds have received much attention as a promising photocatalyst of water splitting for hydrogen production. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

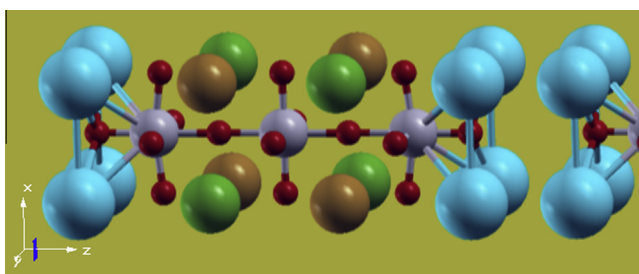


Fig. 2. After interacting with water, the tantalate $K_2LnTa_3O_{10}$, splits along the yellow reference plane shown in Fig. 1. The Potassium adjacent planes separate and shift, and become aligned. The structure becomes layered in the XY plane. Experimentally it is found that the water molecules (not shown in the figure) occupy the space between the Potassium layers [14]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

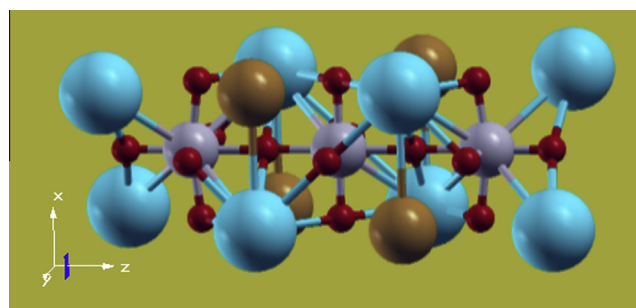


Fig. 3. The Lanthanide atoms (colored in green in Figs. 1 and 2) are removed, and the Potassium atoms take their place. Since only half of the Lanthanide atoms are removed, the cell periodicity is broken, so a doubled cell in the X and Y directions is considered. For visual clarity, the figure shows only the 1×1 cell. This is the general structure that was studied. The space between layers was large enough to ensure that there was no interaction between them. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the latter case, the modification of the electronic structure of these solids could provide a new mechanism for the promotion of electrons to the conduction band. This mechanism could be important in the formation of excitons, which are necessary for the redox process found in photo-catalysis.

2. Method

Ab-initio density functional calculations were performed to calculate the electronic structure of the Tantalum–oxide based compounds $K_2LnTa_3O_{10}$, where Ln refers to a lanthanide atom. Three different atoms were considered for this lanthanide atom: Lanthanum, Praseodymium and Neodymium.

The family of compounds studied has $K_2LnTa_3O_{10}$ as general formula, and corresponds to an Ln-deficient unit cell (one Ln/formula unit), Fig. 1. This figure shows $K_2Ln_2Ta_3O_{10}$, but half of the lanthanide atoms are missing and the nearest Potassium atom occupies their place. When this compound interacts with water it splits along the two Potassium-layers and aligns (Fig. 2). The Ln vacancies are disordered and modelling this is very computationally demanding. Instead the vacancies are considered as alternatively ordered (green spheres in Fig. 2) and the nearest Potassium atoms occupy their places (Fig. 3). It should be noted that in Fig. 2 the green and brown Potassium atoms are now not equivalent and the unit cell is doubled along the x and y directions (not shown).

The WIEN2k code was used to perform the electronic structure calculations, within the framework of the Density Functional Theory. This code is an all-electron scheme which is based on the full-potential (linearized) augmented plane-wave + local orbitals method [18].

It is a known feature of Density Functional Theory that the band gaps calculated using the Kohn–Sham eigen values, are underestimated [19]. To calculate with precision the band gap values, the

GW approximation needs to be used [20] but this was incorporated in an approximated and less computer-consuming way in the modified Becke–Johnson potential (mBJ). The mBJ potential shows an agreement of the same order with the experiment as that obtained with the GW approximation, for wide band gap insulators, $s p$ semiconductors and strongly correlated 3d transition-metal oxides [21,22]. It should be noted that the mBJ potential is still quite computer demanding. The generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) [23] was used for the treatment of the exchange–correlation interactions, after convergence it is substituted by the modified Becke–Johnson potential. This potential converges very slowly requiring many iterations. The criterion for the number of plane waves was $R_{\min}^{MT} \times K^{\max} = 7$, where R^{MT} is the Muffin–Tin radius and K^{\max} is the maximum value of the k plane waves. Within the code used, $R_{\min}^{MT} \times K^{\max}$ is a measure of the quality of the basis set. The number of k -points was 100. These values correspond to a medium quality, and they were chosen in this way due to the use of the mBJ potential. For crystal structure visualization the XCrySDen package [24] was used.

3. Results

The studied system is the layered structure $K_2LnTa_3O_{10}$, with Ln = La, Pr and Nd, after being split by water. The Density of States (DOS) for Ln = La with the PBE functional is given in Fig. 4A, showing a gap of 2.2 eV, while the experimental value is 3.79 eV [14] (Table 1), as mentioned above, the gap is underestimated. Using the modified Becke–Johnson potential (Fig. 4B) a gap of 3.7 eV is obtained, which is much closer to the experimental result. A narrow (localized) La:4f state is above the gap.

We then calculated the density of states for the same layered structure, considering Praseodymium as the lanthanide atom

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