

Energetics and Electronic Structure of Point Defects in NaTaO₃

Minseok Choi¹, Fumiyasu Oba¹, and Isao Tanaka^{1,2}

¹Department of Materials Science and Engineering, Kyoto University, Kyoto, 606-8501, Japan

²Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

Recently, the photocatalytic splitting of water into H₂ and O₂ has been extensively investigated because of a great possibility as a source of clean and renewable hydrogen energy [1]. Perovskite-type sodium tantalate (NaTaO₃) is known to show good photocatalytic activity [2-4]. Especially, La-doped NaTaO₃ was reported to yield very high efficiency for water splitting [2]. To attain such high photocatalytic efficiency, the understanding and control of the defects is very important, because they can affect the catalytic activity, for instance, by acting as recombination centers. To date, however, the physical and chemical properties of the defects in NaTaO₃ have not been well explored, in particular, theoretically.

In this work, we examined lattice vacancies and La impurities in NaTaO₃ through first-principles calculations using density functional theory. The calculations were performed using the plane-wave projector augmented-wave method [5] with the generalized gradient approximation [6] as implemented in the VASP code [7-9]. In perovskite NaTaO₃, the Na ion is located at the twelvefold-coordinated site between the oxygen octahedra and the Ta ion sits at the sixfold-coordinated site corresponding to the center of the oxygen octahedra, as shown in Fig.1. For defect species, the Na and Ta vacancies (V_{Na} and V_{Ta}), the O vacancy (V_O), La at the Na site (La_{Na}), and La at the Ta site (La_{Ta}) were considered. Based on the calculations of the defect formation energies, we elucidated (i) which native defects are likely to form, (ii) which site is preferable for the La impurities, and (iii) how the native defects and the La impurities affect the carrier concentration in La-doped NaTaO₃.

Figure 2 shows the formation energies for the lattice vacancies and the La impurities as a function of the Fermi level. Under oxygen-rich conditions as represented by the oxygen-rich limit considered in the figure, the formation energy of V_{Ta} is very low and negative in a wide range of the Fermi level. Its transition level is close to the valence band maximum, and for the Fermi level above that, the 5- charge state is the most favorable. For V_{Na}, the formation energy is also low, indicating that it is likely to form as well as V_{Ta}, and only the - charge state is stable in the whole range of the Fermi level. Thus, both cation vacancies are shallow acceptors. However, *p*-type NaTaO₃ might be difficult to prepare because V_O, a donor-like defect that can compensate holes, has a lower formation energy for the Fermi level close to the valence band maximum. Under oxygen-poor conditions, V_O has a low formation energy in a wide range of the Fermi level. It shows only the 2+ charge state for any Fermi level within the band gap. This means that V_O plays a role as a double donor and its concentration will be high. However, on account of that the formation energies of V_{Ta} and V_{Na} are lower and are negative when the Fermi level is higher than about 3.4 eV for V_{Ta} and 3.8 eV for V_{Na}, the carrier electrons will be compensated by these cation vacancies. As a result, it is expected to be difficult to grow *n*-type NaTaO₃ with a high carrier concentration.

For La-doped NaTaO₃, La_{Ta} is preferable to La_{Na} in a wide range of the Fermi level under oxygen-rich conditions, and plays a role as an acceptor. La_{Na}, a shallow donor, is more stable than La_{Ta} only in *p*-type regions. In contrast, La_{Na} is likely to form in almost all the range of the Fermi level under oxygen-poor conditions. It is therefore expected that the carrier electron concentration increases as the La concentration increases. In the heavily La-doped case with the Fermi level close to the conduction band minimum, however, La_{Ta} is energetically more favorable. V_{Na} and V_{Ta} can also form spontaneously in such a high *n*-type region. Consequently, a high carrier electron concentration in La-doped NaTaO₃ might be hindered by these defects.

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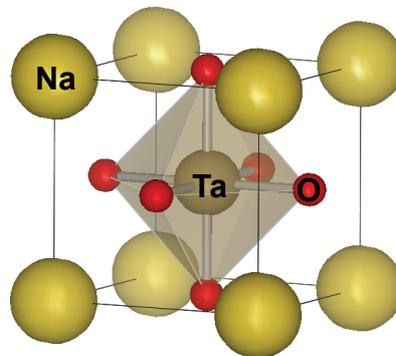


FIG. 1. Crystal structure of NaTaO₃ with the perovskite structure.

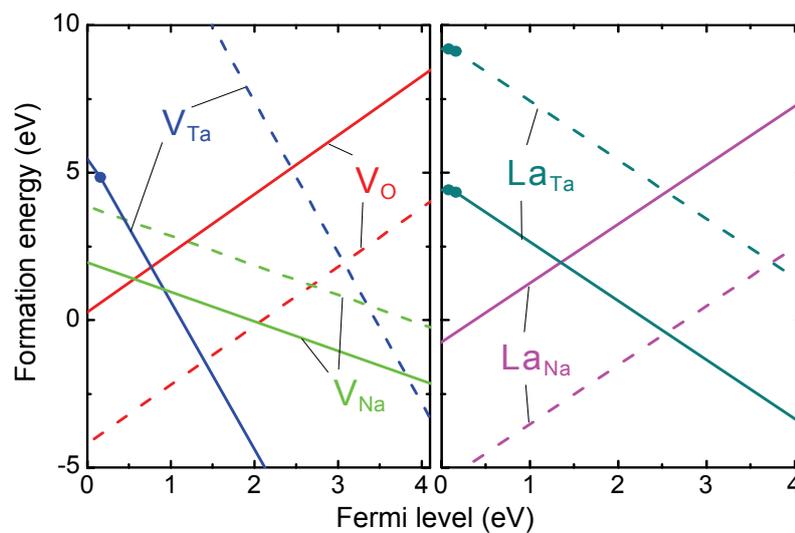


FIG. 2. Formation energies of lattice vacancies (left) and La impurities (right) as a function of the Fermi level. The solid and dashed lines denote the values at the oxygen-rich and oxygen-poor limits, respectively. Transition levels are indicated by the filled circles.