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Published in:
Materials Research Bulletin

DOI:
[10.1016/j.materresbull.2024.113252](https://doi.org/10.1016/j.materresbull.2024.113252)

Publication date:
2025

Document Version
Publisher's PDF, also known as Version of record

[Link to publication](#)

Citation for pulished version (HARVARD):
Javed, F, Zulfiqar, W, Ahmed, S, Abbas, G & Alay-e-Abbas, SM 2025, 'Efficient first-principles evaluation of thermodynamic stability, physical properties and photocatalytic performance of alkali-metal tantalates', *Materials Research Bulletin*, vol. 184, 113252. <https://doi.org/10.1016/j.materresbull.2024.113252>

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Research Papers

Efficient first-principles evaluation of thermodynamic stability, physical properties and photocatalytic performance of alkali-metal tantalates

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ARTICLE INFO

Keywords:

Perovskite oxides
Alkali-metal tantalates
Photocatalysis
Density functional theory
Electronic structure

ABSTRACT

We report the structure, stability, electronic, optical, and photocatalytic properties of sodium and potassium tantalates (NaTaO_3 and KTaO_3) by employing meta-GGA level DFT calculations. Our results show that the structural, mechanical, vibrational, and energetic properties computed using SCAN meta-GGA are in excellent agreement with experimental data compared to earlier calculations performed using semi-local and hybrid-DFT calculations. Moreover, we also show that the employment of TB09 meta-GGA with spin-orbit coupling facilitates reliable description of the electronic properties of NaTaO_3 and KTaO_3 . The optical absorption coefficients of orthorhombic NaTaO_3 and cubic KTaO_3 are also reported and their potential for photocatalytic hydrogen production from overall water molecule splitting has been examined. Our results clearly show that accurate determination of physical properties of NaTaO_3 and KTaO_3 can be achieved by combining SCAN and TB09 meta-GGAs at a significantly lower computational cost compared to computationally demanding hybrid-DFT and GW calculations.

1. Introduction

Increasing demands for energy generation to cater demands of rising populations necessitates a shift to alternative and green fuels as fossil fuels are detrimental to environment and the main cause behind green house effects. For addressing these issues, different energy resources are being explored among which the ones utilizing solar energy are regarded as the most promising for solving environment related problems [1,2]. The technologies utilizing solar energy include solar heating, solar thermal electricity, photovoltaic and photocatalysis, to name a few [3–7]. In particular, the use of solar energy for deriving photocatalytic hydrogen production has gained considerable attention in recent decades as it allows to circumvent the intermittency issues faced by other technologies by producing a green fuel that can be stored and used according to demand [8–12].

Albeit considerable enhancement in our understanding of the mechanistics involved in photocatalytic hydrogen production, commercially viable and efficient photocatalytic materials for efficiently breaking the water molecule for hydrogen production are still needed

[9–12]. In this context, complex oxides are widely believed to be most promising due to their suitable crystal morphologies, easy synthesis and low cost. Although most of these materials generally do not absorb light in the visible portion of the solar spectrum, their tunable electronic properties give them the flexibility for operations in a wide electromagnetic spectrum. Among the most promising complex oxide studied for photocatalytic H_2 production [11], alkali-metal tantalates (i.e. ATaO_3 where $\text{A}=\text{Na}$ and K) adopting perovskite structure have attracted wide attention of the materials research community for their immense potential owing to their high thermal and chemical stability, environment friendly nature, and tunable electronic structure [12–25]. In fact, La-doped NaTaO_3 (NTO) with NiO as co-catalyst has been shown to have the highest photocatalytic yield for splitting of water under UV light irradiation [15]. On the other hand, KTaO_3 (KTO) owing to its stable existence in the prototypical cubic perovskite unit cell and suitably positioned conduction band edge and good dielectric properties is also a highly attractive photocatalyst [26–28].

Since the performance of alkali-metal tantalates during photocatalysis are variously affected by doping [15], presence of excess

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<https://doi.org/10.1016/j.materresbull.2024.113252>

Received 4 September 2024; Received in revised form 1 December 2024; Accepted 6 December 2024

Available online 7 December 2024

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alkali-metal [14], morphology of the particles [19] and the loading of a co-catalyst [14], it is imperative to have an accurate picture of the physical properties of these materials for designing commercially viable photocatalysts for hydrogen production. In this regard, reliable first-principles density functional theory (DFT) calculations can be employed to examine their physical properties independent of any empirical input [29,30]. Although DFT calculations performed at the generalized gradient approximation (GGA) or local density approximation (LDA) level of theory provide structural properties close to experimental data, these semi-local functionals often fall short of correctly predicting the mechanical, dynamical and energetic stability of complex oxides [31]. In addition to determining their stability, the most significant intrinsic factor determining the practical suitability of a photocatalyst is its electronic properties, which directly relates with the photons being absorbed in the material and subsequently converted to chemical or electrical energy [32,33]. The correct band positions of the conduction band minimum (CBM) and valence band maximum (VBM) are very crucial to determine the kind of chemical reaction expected to occur at the surface of a photocatalyst. For this purpose, DFT calculations have been extensively employed to investigate the electronic structures of alkali-metal tantalates [33–42]. However, the calculations performed with GGA and LDA functionals suffer from the derivative discontinuity problem which generally require one to use computationally demanding hybrid-DFT or GW approximation calculations [43–45]. Unfortunately, these schemes are computationally very expensive [46] and are seldom used for supercell calculations exploring the impact of impurities and imperfections on the photocatalytic properties of complex oxides.

As experimental studies performed to investigate the electronic properties of NTO and KTO require theoretical footing for understanding variation in their physical properties [14,16,18,23,47–51], in this work we employ meta-GGA functionals of DFT to show that a combination of these functionals can facilitate reliable exploration of these materials. The strongly constrained and appropriately normed (SCAN) meta-GGA [52] is used for computing the structural, mechanical, dynamical and energetic properties of NTO and KTO. On the other hand, we have employed the TB09 potential functional [53] to compute the electronic, optical and photocatalytic properties of these compounds. Our results clearly show that combining these meta-GGA functionals for evaluating the Photocatalytic properties of NTO and KTO can supplement experimental findings in better accord compared to the results predicted by semi-local functionals of DFT.

2. Computational methods

All of the DFT calculations reported here have been carried out using the WEIN2k computer package which is based on the all electron full-potential linear augmented plane wave plus local orbitals (FP-LAPW+lo) method [54,55]. The FP-LAPW+lo method enables the most accurate calculations for electronic and optical properties of surfaces and crystals. For modeling the crystal potential in the present work, we have used muffin-tin model with atomic radii of 1.75, 1.90, 1.85, and 1.6 for the Na, K, Ta, Nb and O atoms, respectively, along with an energy cut-off of -6.0 Ry for separating the core states from the valence and semi-core states. The plane wave cutoff (R_0K_{max}), maximum value of the wave vector (G_{max}) in the Fourier expansion of charge density and maximum value of angular momentum for the expansion in spherical harmonics within the muffin-tin spheres are chosen to be 8, 24 and 10, respectively. All the calculations are self-consistently converged until a total energy and charge convergence of 10^{-5} Ry and 10^{-3} e is achieved, respectively. Where applicable, the atomic forces on the atoms are minimized to a value less than 1 mRy/a.u. during structural optimizations.

It is well known that the correct prediction of the volume of the unit cell plays a significant role in accurate determination of material's electronic properties. Since larger deviation of the lattice parameters

predicted by GGA and LDA functionals with respect to experimental lattice parameter can result in significant deviation in the computed band gaps [56], we have used the SCAN meta-GGA functional to accurately predict the fully optimized structure of both alkali-metal tantalate. The electronic band gap of the semiconductor materials is a major parameter to predict their photocatalytic properties and for first-principles calculations it strongly depends on the choice of DFT functional used. It has been previously shown that TB09 meta-GGA facilitates accurate electronic band gaps for insulator and semiconductor materials while being computationally inexpensive compared to hybrid-DFT and GW calculations [57]. For this reason, the electronic and optical properties of NTO and KTO, with structural properties fully optimized with SCAN functional, are computed using the TB09 meta-GGA potential functional using the re-optimized parameters suggested by Koller et al. [57]. Since forces are not correctly computed with the inclusion of spin-orbit coupling (SOC) [54], the structural properties and stability of these two compounds are computed without the inclusion of this interaction. On the other hand, the impact of SOC on the calculated electronic structure is systematically examined for both NTO and KTO and the electronic structure computed using SOC is subsequently used for evaluating the electronic, optical and photocatalytic properties of these perovskite oxides. The mechanical properties of both NTO and KTO have been computed using the IRelast software package [58]. On the other hand, the Phonopy code is used to obtain the vibrational properties [59]. For all the vibrational properties computed using the Phonopy code, a force convergence criteria of 0.01 mRy/a.u. has been used in WIEN2k based self-consistent field calculations.

3. Results and discussion

3.1. Atomic structure and energetic stability

While KTO with a Goldschmidt tolerance factor [60] of 1.03 adopts the prototypical cubic perovskite unit cell, the orthorhombic structure of NTO is in accordance with Goldschmidt tolerance factors of 0.94 and also confirmed to be stable in the Pnma phase since our SCAN functional-based calculations predict its energy minima to be -121.907 meV/f.u. below the total energy minima of the Pm-3m phase. For this reason, contrary to earlier DFT studies examining the high temperature cubic perovskite structure of NTO, in this work we have focused on the physical properties of the orthorhombic phase that can be experimentally realized at room temperature [61]. We have constructed the ground state orthorhombic (space group # 62, Pnma) and cubic (space group # 221, Pm-3m) conventional unit cells of NTO and KTO, respectively, which are shown in Fig. 1. Complete optimization of these crystal structures has been performed using the SCAN meta-GGA functionals. Unlike the cuboctahedral coordination of O atoms with K in cubic KTO having similar K–O bond length of 2.818 Å, there are eight O atoms coordinated with Na atom in NTO with Na–O bond lengths ranging between 2.351 Å to 2.736 Å. Owing to reduced coordination of the Na atoms with O in the Pnma phase of NTO, the TaO₆ octahedra are oppositely tilted along a- and b-axis with the same magnitude (see Fig. 1) such that the Ta–O bond lengths of Ta with apical and equatorial O atoms are slightly different compared to one Ta–O bond length in cubic KTO.

For evaluating the energetic stability of alkali-metal tantalates, the crystal volumes of both compounds and the internal geometries of NTO are completely optimized with SCAN functionals to obtain the ground state total energies. In addition, the elemental solids (Na, K and Ta), oxygen molecule (O₂) and the relevant binary oxides (i.e. Na₂O, K₂O and Ta₂O₅) have also been optimized with SCAN functional as these systems are important in determining the thermodynamic stability of NTO and KTO in their respective phases. The ground state lattice parameters and atomization energies of Na, K and Ta metal along with the bond length of an oxygen molecule and its atomization energy are presented in Table 1. Comparing the results computed using SCAN in this work with

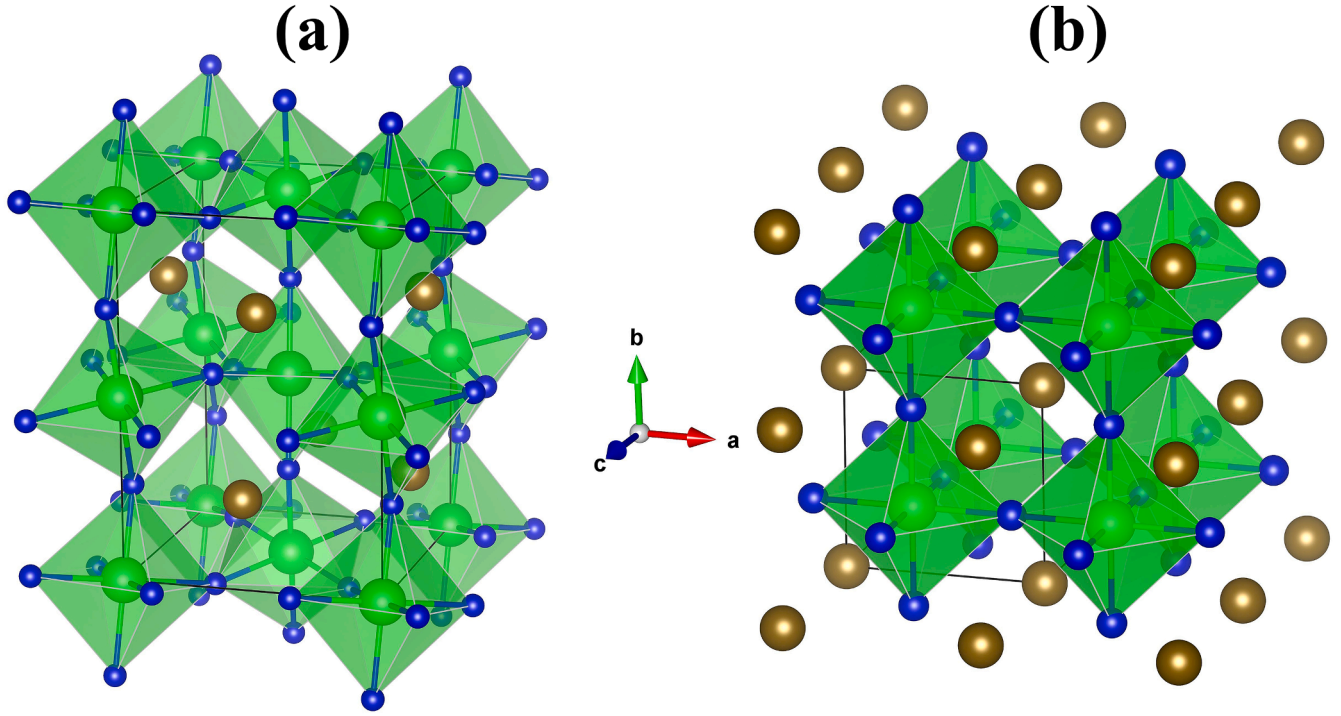


Fig. 1. Crystal structures of orthorhombic (space group # 62, Pnma) NaTaO₃ and cubic KTaO₃ (space group # 221, Pm-3m) showing the conventional unit cell (solid black line) and anion coordination polyhedras for the TaO₆ octahedra (green shaded area). The alkali-metal, tantalum and oxygen atoms are represented by brown, green and blue spheres, respectively.

Table 1

Structural properties (Å) and cohesive energies (eV/atom) of the ground state crystal structures of Na (body-centered cubic), K (body-centered cubic) and Ta (body-centered cubic) and O₂ molecule computed using SCAN meta-GGA functional compared with earlier GGA based DFT results and experimental data.

System	SCAN This work	GGA Other DFT works	Experiment
Na (Im-3m)			
a_0	4.204	4.197 ⁶⁴	4.290 ⁶⁸
E_c	-1.065	-1.090 ⁶⁵	-1.113 ⁶⁹
K (Im-3m)			
a_0	5.315	5.271 ⁶⁴	5.320 ⁷⁰
E_c	-0.794	-0.870 ⁶⁶	-0.934 ⁶⁹
Ta (Im-3m)			
a_0	3.276	3.320 ⁶⁴	3.300 ⁷¹
E_c	-8.486	-8.110 ⁶⁶	-8.100 ⁶⁹
O ₂ molecule			
r_0	1.218	1.219 ⁶⁷	1.210 ⁷²
E_c	-2.756	-2.975 ⁶⁷	-2.560 ⁷²

experimental data clearly indicates the better performance of this meta-GGA compared to GGA based calculations reported earlier [62–70].

In order to evaluate the stability of NTO and KTO with respect to their respective competing phases, we have also used SCAN meta-GGA functional to optimize their ground state unit cells for which the results are shown in Table 2. While both Na₂O and K₂O are stable in the Fm-3m phase, earlier studies have predicted Pmmn phase of Ta₂O₅ to be energetically more stable [71] compared to the experimentally observed Pmmm phase [72]. For this reason the enthalpies of formation of Na₂O, K₂O, Ta₂O₅ (Pmmm) and Ta₂O₅ (Pmmn) unit cells are computed using the formulas

$$\Delta H_f[\text{Na}_2\text{O}]^{\{\text{Fm}\bar{3}\text{m}\}} = E_t^{\text{Na}_2\text{O}} - 2E_t^{\text{Na}} - \frac{1}{2}E_t^{\text{O}_2} \quad (1)$$

$$\Delta H_f[\text{K}_2\text{O}]^{\{\text{Fm}\bar{3}\text{m}\}} = E_t^{\text{K}_2\text{O}} - 2E_t^{\text{K}} - \frac{1}{2}E_t^{\text{O}_2} \quad (2)$$

Table 2

Lattice parameters (Å) and enthalpies of formation (eV/f.u.) of Na₂O, K₂O and Ta₂O₅ computed using the SCAN meta-GGA functional compared with earlier GGA based DFT results and experimental data.

Compound	SCAN This work	GGA Other DFT works	Experiment
Na ₂ O (Fm-3m)			
a_0	5.480	5.595 ⁷³	5.550 ⁷⁶
ΔH_f	-4.186	-4.350 ⁷³	-4.332 ⁷⁵
K ₂ O (Fm-3m)			
a_0	6.346	6.488 ⁷³	6.436 ⁷⁶
ΔH_f	-3.613	-3.759 ⁷³	-3.764 ⁷⁵
Ta ₂ O ₅ (Pmmm) *			
a_0	3.660	3.700 ⁷³	3.678 ⁷⁴
b_0	3.852	3.892 ⁷³	3.896 ⁷⁴
c_0	6.439	6.527 ⁷³	6.225 ⁷⁴
ΔH_f	-19.042	-21.196 ⁷³	-21.236 ⁷⁵
Ta ₂ O ₅ (Pmmn) **			
a_0	12.996	3.871 ⁷³	–
b_0	3.824	3.904 ⁷³	–
c_0	3.857	13.128 ⁷³	–
ΔH_f	-21.360	-23.464 ⁷³	–

* experimentally observed phase.

** theoretically predicted stable phase.

$$\Delta H_f[\text{Ta}_2\text{O}_5]^{\{\text{Pmmm}\}} = E_t^{\text{Ta}_2\text{O}_5} - 2E_t^{\text{Ta}} - \frac{5}{2}E_t^{\text{O}_2} \quad (3)$$

$$\Delta H_f[\text{Ta}_2\text{O}_5]^{\{\text{Pmmn}\}} = E_t^{\text{Ta}_2\text{O}_5} - 4E_t^{\text{Ta}} - \frac{10}{2}E_t^{\text{O}_2} \quad (4)$$

where E_t are the minimum total energies of structurally optimized unit cell/molecule. From Table 2 one can see that the SCAN meta-GGA calculated lattice parameters of the binary oxides in this work are in good agreement with experimental data and do not show large over-estimation of crystal volume (e.g. maximum $(V^{\text{expt.}} - V^{\text{SCAN}})/V^{\text{expt.}} = 1.769\%$ for Ta₂O₅) commonly observed for GGA calculations (e.g. $(V^{\text{expt.}} - V^{\text{GGA}})/V^{\text{expt.}} = 5.370\%$ for Ta₂O₅). On the other hand, the

enthalpies of formation computed using SCAN functional show slight underbinding which is contrary to the overbinding effect seen in GGA results. Nevertheless, the enthalpies of formation computed using the meta-GGA show good accord with experimental data [72–74] and also predict Pmmn phase of Ta₂O₅ to be the most stable. It is interesting to note from Table 2 that the enthalpy of formation predicted by SCAN meta-GGA for Pmmn phase of Ta₂O₅ is closer to the experimental value [73]. This together with the data on the reaction energies computed using SCAN meta-GGA (discussed below) suggests that further experimental studies on the low temperature phases of Ta₂O₅ is necessary to confirm its most stable orthorhombic phase.

In order to determine the synthesis feasibility of NTO and KTO with reference to their competing elemental phases (i.e. Na, K, Ta and O₂), we have computed the enthalpy of formation for the unit cells of these two systems using the formulas

$$\Delta H_f[\text{NaTaO}_3]^{(\text{Pnma})} = E_t^{\text{NaTaO}_3} - 4E_t^{\text{Na}} - 4E_t^{\text{Ta}} - \frac{12}{2}E_t^{\text{O}_2} \quad (5)$$

$$\Delta H_f[\text{KTaO}_3]^{(\text{Pnma})} = E_t^{\text{KTaO}_3} - E_t^{\text{K}} - E_t^{\text{Ta}} - \frac{3}{2}E_t^{\text{O}_2} \quad (6)$$

In addition, we have also determined the stability of NTO and KTO with respect to (w.r.t) their competing binary oxides in terms of the reaction energy, which can be defined as the difference of the total energies of ternary oxide and the sum of total energies of the binary oxides containing equivalent atoms. For the alkali-metal tantalate considered in the present study, we can express reaction energy with the formula

$$E^{\text{react}} = E_t^{\text{ATaO}_3} - \frac{(E_t^{\text{A}_2\text{O}} - E_t^{\text{Ta}_2\text{O}_5})}{2} \quad (7)$$

where E_t are the minimum total energies of fully optimized unit cells, while A = Na or K. The calculated lattice parameter of NTO ($a_0 = 5.444$ Å, $b_0 = 7.755$ Å and $c_0 = 5.510$ Å) and KTO ($a_0 = b_0 = c_0 = 3.986$ Å) clearly indicate that SCAN meta-GGA circumvents the overestimation of lattice volume by GGA and predicts structural properties in good accord with experiment [75,76]. It is also evident from Table 3 that the experimental enthalpies of formation for alkali-metal tantalates [77,78] are slightly smaller than our calculated enthalpies of formation. Nevertheless, one can see that the orthorhombic and cubic crystal structures of NTO and KTO, respectively, are predicted to be thermodynamically stable. This is evident since not only the enthalpies of formation predicted by SCAN meta-GGA confirm the stability criteria $\Delta H_f^{\text{ABO}_3} \leq \Delta H_f^{\text{A}_2\text{O}} + \Delta H_f^{\text{Ba}_2\text{O}_5}$, the reaction energies listed in Table 3 for both Pmmm and Pmmn phases of Ta₂O₅ also confirm that these systems are energetically stable.

Table 3

Lattice parameters (Å), enthalpies of formation (eV/f.u.) and reaction energies (eV/f.u.) of NaTaO₃, and KTaO₃ computed using the SCAN meta-GGA functional compared with earlier GGA based DFT results and experimental data.

Compound	SCAN This work	GGA Other DFT works	Experiment
NaTaO ₃ (Pnma)			
a_0	5.444	5.530 ⁷³	5.477 ⁷⁷
b_0	7.755	7.870 ⁷³	7.789 ⁷⁷
c_0	5.510	5.584 ⁷³	5.521 ⁷⁷
ΔH_f	-14.466	-15.400 ⁷³	-14.282 ⁷⁸
$E^{\text{react.}}$ (w.r.t Pmmm)	-2.852	-2.627 ⁷³	-1.527 ⁷⁸
$E^{\text{react.}}$ (w.r.t Pmmn)	-1.693	-1.493 ⁷³	–
KTaO ₃ (Pm-3m)			
a_0	3.986	4.031 ⁷³	3.988 ⁷⁹
ΔH_f	-14.626	-15.435 ⁷³	-14.595 ⁸⁰
$E^{\text{react.}}$ (w.r.t Pmmm)	-3.298	-2.958 ⁷³	2.110 ⁸⁰
$E^{\text{react.}}$ (w.r.t Pmmn)	-2.139	-1.824 ⁷³	–

3.2. Mechanical properties

First-principles calculation based determination of elastic constants of a material is one of the most valuable outcome of electronic structure methods which allow confirming the mechanical stability of crystal structures. Among the available DFT methods, the computation of elastic constants within the WIEN2k code can be performed using IRelast package which gives information concerning important mechanical properties such as Bulk modulus, Shear modulus, Young's modulus and Poisson's ratio. In case of the cubic perovskite crystal structure of KTO, there are three independent elastic constants, namely C_{11} , C_{12} and C_{44} [79]. According to the Born stability criteria, a cubic crystal is mechanically stable when the elastic constants satisfy the conditions [80]

$$C_{44} > 0; C_{11} - C_{12} > 0; C_{11} + 2C_{12} > 0 \quad (8)$$

simultaneously. Contrary to the case of cubic perovskite, the orthorhombic Pnma phase perovskite crystal structure of NTO has nine independent elastic constants C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} , and C_{66} [79]. For NTO to be mechanically stable in the orthorhombic Pnma phase, these nine elastic constants are required to simultaneously satisfy the following conditions [80]

$$C_{11} > 0; C_{44} > 0; C_{55} > 0; C_{66} > 0; C_{11}C_{22} > C_{12}^2; C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \quad (9)$$

The elastic constants of NTO and KTO computed using the SCAN meta-GGA functionals are presented in Table 4 together with available experimental [81] and theoretical data. It is clear that the values computed in this work satisfy the mechanical stability conditions for the cubic and orthorhombic structures defined in Eqs. (8) and (9), respectively, confirming that the respective phases of KTO and NTO are stable. It is also interesting to note that the values of elastic constants computed using SCAN meta-GGA for KTO are in better agreement with experimental data [82]. While GGA level DFT calculation of mechanical properties for materials adopting the perovskite structure also provide reasonable agreement with experimental data [83–85], it is clear from Tables 4 and 5 that the SCAN functional can be efficiently employed in place of computationally expensive HSE06 calculations [44].

Using the Hill approximation [86], the Bulk modulus (B), Shear modulus (G), Young's modulus and Poisson's ratio for NTO and BTO have been obtained from the Voigt and Reuss formalism [87,88,31,89] using the elastic constants predicted by SCAN meta-GGA in Table 4. The Bulk modulus of NTO and KTO obtained from elastic constants listed in Table 4 are presented in Table 5 together with the Bulk modulus determined by fitting the total energy vs volume data to Birch-Murnaghan equation of state [90]. The close comparison of the two values of Bulk modulus confirm that the elastic constants obtained from IRelast package reliably confirm the mechanical stability of the two perovskite materials. Table 5 shows that both NTO and KTO have similar values of Shear modulus ($G \sim 137$ GPa) which indicates that both these systems are capable to resist against the shear deformation with similar outcomes. Similarly, the Bulk modulus for both NTO ($B = 226.600$ GPa) and KTO ($B = 211.176$ GPa) indicate that these systems have similar hardness and will show equivalent resistance against plastic deformation. The calculated values of Young's modulus for NTO ($Y = 343.359$ GPa) and KTO ($Y = 339.832$ GPa) in this work together with the close comparison of KTO's mechanical properties with experimental data confirm the qualitatively equal stiffness of the two systems against longitudinal stress. On the other side, both these alkali-metal tantalates are brittle in nature as the calculated value of ν for these materials is less than the critical value of 0.26. Poisson's ratio can also be used to determine the bonding nature of a compound. Since the calculated values of ν are all less than 0.25 in Table 5, both the materials are predominantly covalent in their bonding characteristics. All in all, the close comparison of experimental values of Bulk modulus, Shear modulus and Young's modulus with our computed SCAN meta-GGA results clearly

Table 4

Elastic constants (GPa) of orthorhombic NaTaO₃ and cubic KTaO₃ calculated using the SCAN meta-GGA functional. For comparison, available experimental and theoretical data are also provided.

Compound	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
NaTaO₃									
SCAN	399.067	80.952	192.344	502.870	92.888	405.527	104.552	209.296	100.780
KTaO₃									
SCAN	470.070	81.730	–	–	–	–	109.421	–	–
GGA	420.280 ⁴⁶	76.600 ⁴⁶	–	–	–	–	99.840 ⁴⁶	–	–
HSE06	470.730 ⁴⁶	86.940 ⁴⁶	–	–	–	–	111.590 ⁴⁶	–	–
Experiment	431 ⁸⁷	103 ⁸⁷					109 ⁸⁷		

Table 5

The Bulk modulus B (GPa), Shear Modulus G (GPa), Young's Modulus Y (GPa) and Poisson's ratio ν of orthorhombic NaTaO₃ and cubic KTaO₃ calculated using the SCAN meta-GGA functional. For comparison, available experiment and theoretical data are also provided.

Compound	B	G	Y	ν
NaTaO₃				
SCAN	226.600 (230.679)*	137.624	343.359	0.247
KTaO₃				
SCAN	211.176 (215.341)*	137.942	339.832	0.231
GGA	191.160 ⁴⁶	124.290 ⁴⁶	306.450 ⁴⁶	0.233 ⁴⁶
HSE06	214.870 ⁴⁶	138.870 ⁴⁶	342.760 ⁴⁶	0.234 ⁴⁶
Experiment	212.330 ⁸⁷	128.440 ⁸⁷	320.670 ⁸⁷	0.248 ⁸⁷

* bulk modulus obtained from energy vs volume curve fitted to Birch-Murnaghan equation of state.

show an excellent performance of this functional in determining the mechanical stability of these perovskite oxides.

3.3. Vibrational properties

Vibrational properties of any solid can be estimated by phonons, representing the quantized vibration of atoms in a solid [91]. Apart from gaining significant attention in indicating the phase transition and phase stability, phonons also play an important role in modulating the transport properties of materials [92,93]. Since vibrational properties are closely related with phonon mediated optical transitions, a better understanding of phonon modes of a perovskite can be important in determining its photocatalytic performance. Moreover, phonons play a vital role in controlling the ferroelectric and dielectric properties of perovskite materials and they are modified by a variation in the temperature or stress [94,95]. First-principles calculations allow to estimate the instabilities and experimentally reported phonon modes. However, both hybrid and semi-local functionals are unable to accurately describe the phonon properties [31]. Benrekia et al., performed first-principles VASP calculations on cubic KTaO₃ perovskite by employing the HSE, PBEsol and PBE functionals and found the ferroelectric instabilities for all functionals expect PBEsol functional [96]. On the other hand, the ferroelectric instability for KTO was not observed with local density approximation [97].

Since the lattice parameters can modify the vibrational properties of the perovskite material [97], it is very important to use accurate value of the lattice parameter for phonon calculations. Table 3 clearly shows that the lattice parameters computed using the SCAN meta-GGA functional are in the excellent agreement with the available experimental data [98, 99]. Therefore, the SCAN meta-GGA functional is used here to obtain the vibrational properties of alkali-metal tantalate. Keeping in view the differences in crystal structures and a large number of calculations required for orthorhombic phase of NTO, we have computed the phonon band structures using $1 \times 1 \times 1$ and $2 \times 2 \times 2$ supercells of NTO and KTO, respectively, using the phonopy code. The calculated phonon band structures of these two systems along selected high symmetry points are presented in Figure S1 in the supplementary information. In order to compare the performance of different DFT functional in reproducing

phonon properties of the studied perovskites, we have listed the calculated phonon frequencies in Table 6. It is worth pointing out here that for cubic KTO there are five triply degenerate phonon modes at the Γ point. Among these, there are four optical phonons and one acoustic phonon. The four triply degenerate phonon modes at Γ point have non-zero frequency and three of these four triply degenerate optical phonons are infrared active that are denoted by TO1, TO2 and TO3.

A comparison between the performance of various DFT functionals in predicting the vibrational properties of alkali-metal tantalates perovskites can be made on the basis of optical phonon frequencies at the Γ symmetry point. From Table 6, it can be seen that the Γ point phonon frequencies calculated by employing the SCAN meta-GGA functional for both NTO and KTO are in accordance with the experimental data. While theoretical data on the phonon frequencies for NTO is scarce, we can also see from Table 6 that the PBE GGA based DFT calculations for KTO inaccurately predict [96] this material to be dynamically unstable. This problem persists even for the more reliable HSE based DFT calculations reported in Ref. [96]. However, the SCAN meta-GGA based calculations performed in the present work not only reproduce dynamical stability of cubic KTO there is also no ferroelectric transition for this system in accordance with experiments [97].

3.4. Electronic properties

By using the lattice parameters computed using the SCAN functional, we have calculated the electronic band structures and density of states of the NTO and KTO. It is well known that the structural and energetic properties of solids computed with and without the inclusion of SOC are not different since the contribution to total energy from this interaction can be separated into atomic contributions [100]. However, for an accurate description of the electronic band dispersions of alkali-metal tantalates, the inclusion of SOC may be necessary owing to the presence of Ta in these perovskites. Our results indicate that the inclusion of SOC does have a noticeable impact on the electronic band located near the Fermi energy (E_F). A comparison of the electronic band structure diagrams of NTO and KTO computed with and without the inclusion of SOC in SCAN meta-GGA calculations (see Figure S2 in the supplementary information) clearly demonstrate small variations in the band gaps.

Table 6

Calculated optical phonon frequencies (THz) for the orthorhombic and cubic crystal structures of NaTaO₃ and KTaO₃ computed using the SCAN meta-GGA functional along with available theoretical and experimental data. Imaginary frequencies are indicated with a '-' sign.

Compound	SCAN This work	GGA Other works	HSE Other works	Experiment
NaTaO₃				
TO1	2.179	–	–	2.882 ¹⁰⁰
TO2	3.487	–	–	4.173 ¹⁰⁰
TO3	4.591	–	–	4.651 ¹⁰⁰
KTaO₃				
TO1	3.861	-2.248 ⁹⁸	-1.529 ⁹⁸	2.428 ¹⁰¹
TO2	5.804	5.636 ⁹⁸	6.086 ⁹⁸	5.966 ¹⁰¹
TO3	16.829	14.960 ⁹⁸	15.799 ⁹⁸	16.369 ¹⁰¹

Therefore, all the electronic, optical and photocatalytic properties discussed here are computed with the inclusion of SOC.

Figs. 2 & 3 display the electronic band structure diagrams and partial density of states (PDOS) plots for NTO and KTO computed using SCAN and TB09 meta-GGA functionals with the inclusion of SOC interaction. Despite its good performance in predicting the structural and energetic properties of the perovskites under consideration, it is evident from the band structure diagrams shown in Figs. 2 & 3 that the SCAN functional underestimates the band gap compared to TB09 meta-GGA. While the overall characteristics of the electronic density of states for NTO and KTO obtained using the two meta-GGAs in this work appear to be similar, there are noticeable differences in the contribution of atoms in PDOS plots which can be attributed to the better description of the exchange potential by TB09 functionals. From Fig. 2 it is evident that the upper valence band for NTO gets a major contribution from the 2p states of two inequivalent O atoms along with a small contribution coming from the Ta-5d states. Similarly, the occupied energy states of KTO in Fig. 3 also show clear dominance O-2p states irrespective of the choice of the functionals used. However, comparison of the PDOS plots computed using SCAN and TB09 functionals clearly shows that the contribution of O-2p states in the valence band predicted by the later meta-GGA is slightly enhanced that can be attributed to the modified Becke-Johnson exchange potential of TB09 functional. Irrespective of the choice of the functional, it can be seen that the conduction band for both NTO and KTO is basically made of Ta-5d states along with a minor contribution coming from the O-2p states. The negligible contribution of O-2p orbitals in the conduction band of NTO and KTO is also confirmed from the band character plots shown in Figure S3 (supplementary information file) where one can see clear dominance of Ta-5d orbitals. Interestingly, the application of TB09 meta-GGA appears to have an opposite impact on the overall features of conduction bands of NTO and KTO. Comparing

of the band structures and PDOSs plots of Fig. 2 indicates that the TB09 meta-GGA separates the electronic states above E_F into two separate bands for the orthorhombic NTO. On the contrary, the application of TB09 meta-GGA on cubic KTO causes the small overlap of the conduction band states around 7 eV above the E_F computed using SCAN functional to increase and eliminate the minima of PDOS observed in Fig. 3 (b). In addition, it is also evident from Figs. 2 & 3 that SCAN meta-GGA predicts that the Na-3s and K-4s states have slightly large contribution in the upper conduction band compared to TB09. However, comparison of the two PDOS plots computed using TB09 meta-GGA shown in Figs. 2 & 3 shows that the reduction in the contribution of Na-3s states is more pronounced in the PDOS of NTO than the reduction of K-4s states in the PDOS of KTO.

From the electronic properties of NTO presented in Fig. 2, it can be seen that the optical band gap between the Ta atom's 5d states in the conduction band edge and O-2p states in the valence band edge is along the $\Gamma - \Gamma$ symmetry direction. On the other side, the fundamental band gap for KTO is smaller than the optical band gap, which is along the $R - \Gamma$ symmetry direction. The SCAN and TB09 computed band gaps for alkali-metal tantalate studied in this work are presented in Table 7 along with experimental data and theoretical band gaps predicted by PBE, HSE06 and GW approximation. It is worth to mentioning here that, SCAN meta-GGA functional used in our study underestimates energy band gaps. In previous studies, the band gap underestimation by GGA functional has been shown to be overcome only by employing beyond-DFT calculations. As it is evident from the Table 7 that Liu et al. [45] Wang et al. [43] and Xu et al. [44] employed hybrid-DFT and GW approximation for obtaining band gaps in good agreement with experimental data. In the present work, on the other hand, we have computed the electronic band gaps with TB09 meta-GGA functional for both NTO ($E_g = 4.328$ eV) and KTO ($E_g = 4.260$ eV) which show excellent agreement with both GW and

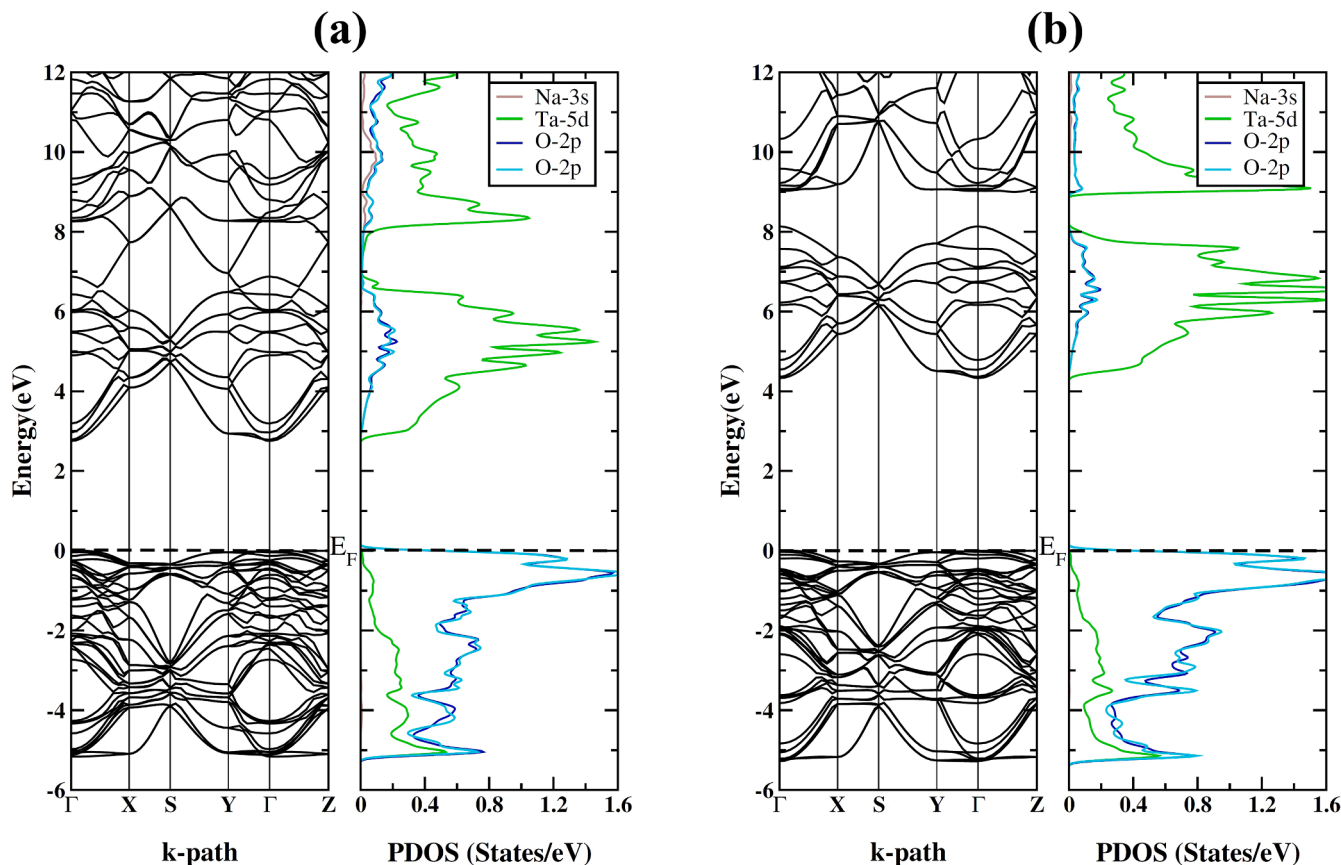


Fig. 2. The calculated electronic band structure diagrams and partial density of states (PDOS) plots (PDOS) for NaTaO₃ computed using (a) SCAN and (b) TB09 meta-GGA functionals with the inclusion of SOC interactions. The Fermi energy (E_F) is indicated by the black dashed line.

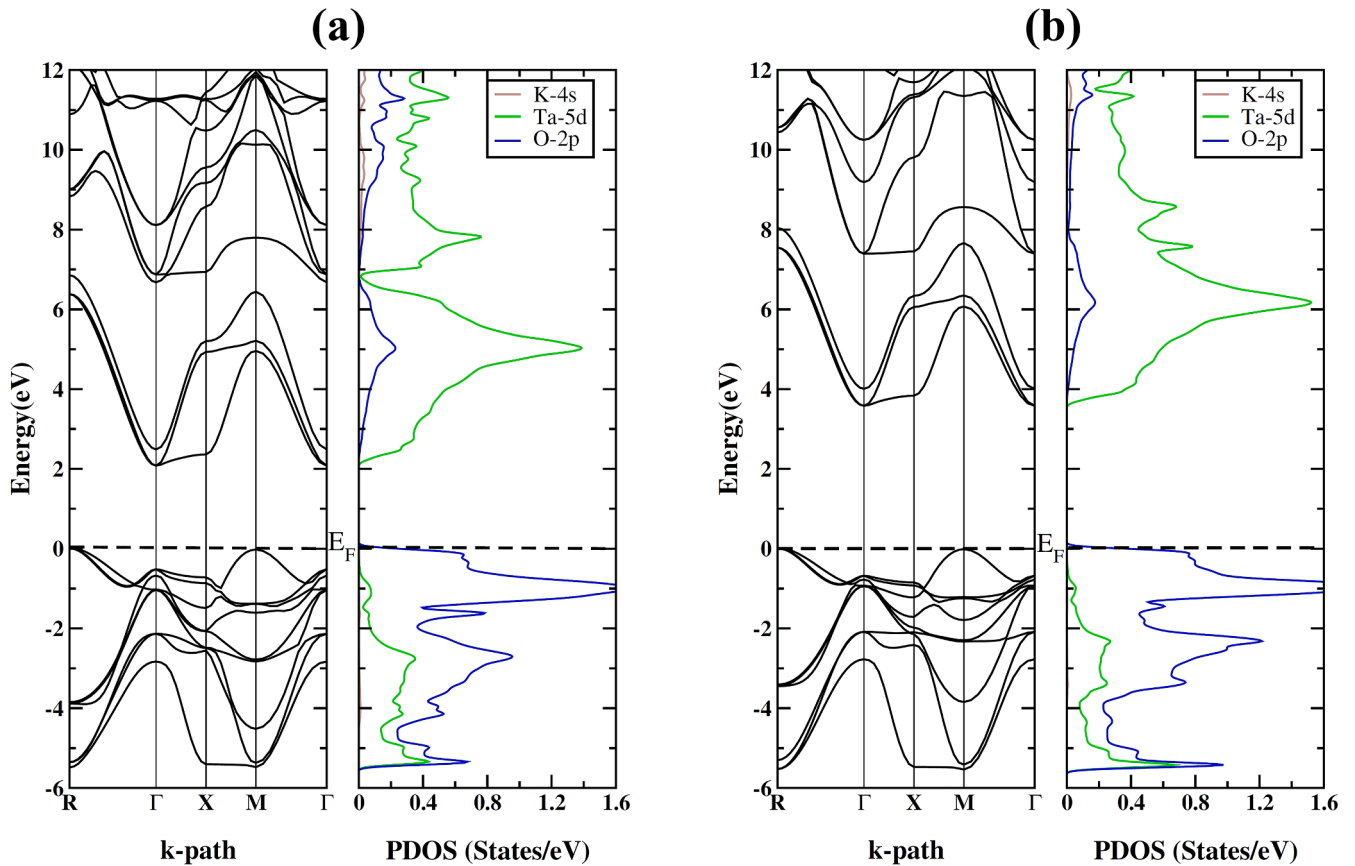


Fig. 3. The calculated electronic band structure diagrams and partial density of states plots for KTaO₃ computed using (a) SCAN and (b) TB09 meta-GGA functionals with the inclusion of SOC interactions. The Fermi energy (E_F) is indicated by the black dashed line.

Table 7

The calculated direct ($\Gamma - \Gamma$) and indirect ($R - \Gamma$) gaps (in eV) of NaTaO₃ and KTaO₃. Values computed using the SCAN and TB09 meta-GGAs in this work are compared with theoretical data computed using PBE, hybrid-DFT and GW approximation and experimental band gaps.

Compound	E_g (eV)					
	SCAN This work	TB09 This work	PBE Others	HSE06 Others	GW Others	Experiment
NaTaO ₃						
$\Gamma - \Gamma$	2.751	4.328	2.650 47	4.000 47	4.280 45	4.350 ⁵¹
KTaO ₃						
$\Gamma - \Gamma$	2.595	4.260	2.740 46	4.300 46	4.330 46	4.350 ⁷⁷
$R - \Gamma$	2.078	3.580	2.110 46	3.640 46	3.510 45, 3.730 46	3.640 ⁷⁷ , 3.757 ⁵¹

experimental band gaps. As far as the small differences in the values of the band gaps are concerned, it is worth pointing out here that the GW approximation results are fundamental band gaps, while the experimental band gaps are obtained from optical spectral measurements by considering the polaronic and excitonic effects which play a significant role. Thus, the absence of these effects in the TB09 and GW approximation may lead to differences between theoretical and experimental band gaps. In addition, the accuracy of the outcomes of theoretical techniques is strongly dependent on the calculation parameters and

computational time that also shows influence on the reliability of the first-principles calculations. Nevertheless, given that the TB09 functional is semi-local in nature and computationally less expensive than GW and hybrid-DFT calculations makes it an efficient candidate for examining electronic, optical and photocatalytic properties of materials, which is evident from the values reported in Table 7.

3.5. Optical properties

To enhance our knowledge about the photocatalytic performance of alkali-metal tantalates, it is crucial to investigate the optical properties of these compounds which gives us valuable insights about how these compounds respond in response to incident electromagnetic radiations. However, only a few efforts have been made to study the optical properties of NTO and KTO perovskites materials. Optical absorption can be regarded as one of the basic parameter to investigate the potential of a semiconductor material for solar driven water splitting. The most important information obtained from optical absorption spectrum is the wavelength of electromagnetic radiation required for the generation of holes and electrons [83,101]. Since the experimental band gaps of NTO and KTO are greater than 3 eV, these materials can be useful for photovoltaic devices operating in the ultraviolet region of the electromagnetic spectrum. Using the independent particle approximation (IPA) based *optic* module of WIEN2k code [55], in this work we examine the optical properties of NTO and KTO by computing the complex dielectric tensor $\epsilon(\omega) = \text{Re}\epsilon(\omega)_{ij} + i \text{Im}\epsilon(\omega)_{ij}$ [102] as a function of incident photon energy with both SCAN and TB09 meta-GGA functionals. The imaginary part of the complex dielectric tensor can be defined in terms of the conduction ($|c_k\rangle$) and the valence ($|v_k\rangle$) eigenstates with the formula [102]

$$\text{Im}\epsilon(\omega)_{ij} = \frac{4\pi e^2}{m^2 \omega^2} \sum_{c,v} \int dk \langle c_k | p^i | v_k \rangle \langle v_k | p^j | c_k \rangle \delta(E_{ck} - E_{vk} - \omega) \quad (10)$$

while the real part of the complex dielectric tensor can be defined [102]

$$\text{Re}\epsilon(\omega)_{ij} = \delta_{ij} + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \text{Im}\epsilon(\omega')_{ij} d\omega'}{\omega'^2 - \omega^2} \quad (11)$$

For a particular crystallographic direction, the above values of $\text{Re}\epsilon(\omega)_{ii}$ and $i \text{Im}\epsilon(\omega)_{ii}$ can be used to obtain the absorption coefficients with the formula

$$A(\omega)_{ii} = \frac{\omega}{c} \sqrt{2(|\epsilon(\omega')_{ii}| - \text{Re}\epsilon(\omega')_{ii})} \quad (12)$$

This means that the cubic crystals have similar absorption coefficients in all crystallographic directions, while the absorption coefficients for orthorhombic system differ along all three lattice directions. In Fig. 4, the SCAN and TB09 calculated wavelength dependent absorption coefficients of NTO are shown parallel to a_0 lattice parameter (xx). From Figure S4, it can be seen that the variation of absorption coefficients along b_0 and c_0 are slightly different. Nevertheless, these variations only influence the variation of absorption coefficients while leaving the threshold in the absorption coefficients almost similar. A comparison of the absorption coefficients computed using SCAN and TB09 functionals in Fig. 4 clearly show that NTO can absorb photons with wavelengths < 450 nm and < 285 nm, respectively. However, since the band gap computed using TB09 functional agrees with experimental data, it is evident that pristine NTO can only be used for photocatalysis in the UV region. The better performance of the TB09 functional in predicting optical properties of NTO are also in accord with experimental photocatalysis observed in this material [13] where a high pressure mercury lamp with photon energy of 270 nm was used.

The absorption coefficients for cubic KTO are presented in Fig. 5 where one can again notice that the SCAN meta-GGA incorrectly predicts that the visible light photons can be absorbed in this material. However, the absorption coefficients obtained from the electronic structure of KTO computed using TB09 correctly indicates that photons below < 346 nm would not be absorbed in this perovskite oxide. Since the direct band gap of KTO predicted by TB09 is slightly larger (4.260 eV), one can see that the absorption of photons with wavelength < 290 nm can be realized in experiments. In fact, this is in good accord with experimental studies in photocatalytic performance of KTO performed under irradiation with UV light [14]. All in all, the optical properties computed using the TB09 meta-GGA functionals confirm that the optical absorption threshold for NTO and KTO lies in the UV region of the electromagnetic spectrum.

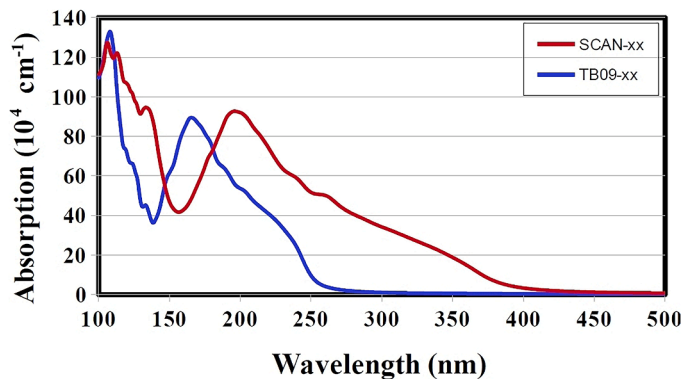


Fig. 4. The calculated absorption coefficient for orthorhombic NaTaO₃ parallel to a_0 lattice parameter (xx) computed using the SCAN (red lines) and TB09 (blue line) meta-GGA functionals.

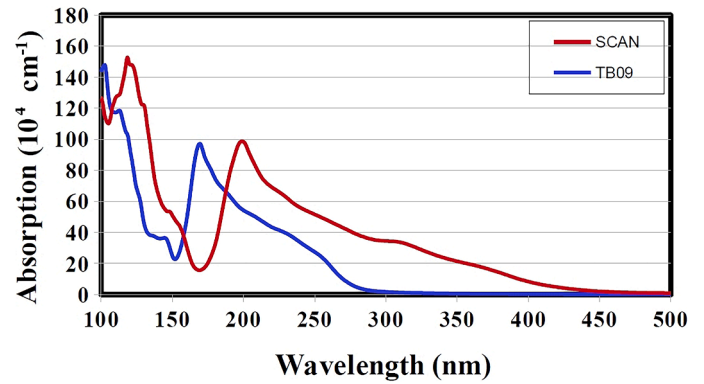


Fig. 5. The calculated absorption coefficient for cubic KTaO₃ computed using the SCAN (red lines) and TB09 (blue line) meta-GGA functionals.

3.6. Photocatalytic performance

Although the optical absorption plots presented in Figs. 4 & 5 show that NTO and KTO are active in the UV region, the application of these materials in photocatalytic water splitting demands that the band edge potentials should be positioned appropriately with respect to redox potentials required for decomposition of the water molecule. For the production of hydrogen through water splitting, a photocatalyst should have its valence band's edge potential more positive than the redox potential of H₂O/O₂. Similarly, the conduction band's edge potential should be more negative than the redox potential of H⁺/H₂ [103]. We have computed the band edge potentials of NTO and KTO by employing the procedure described in Refs. [104–106]. For the sake of comparison the direct band gaps of SCAN and TB09 computed in this work and the direct experimental band gaps reported Refs. [49,75] are used for computing the band edge potentials which are shown in Fig. 6. For the case of NTO, the conduction and valence band potentials obtained from TB09 functional are located -1.219 eV above the H⁺/H₂ redox potential and 1.879 eV below the H₂O/O₂ redox potential, respectively. Compared to this, the underestimated band gap of SCAN meta-GGA predicts conduction and valence band potentials to be located -0.430 eV above the H⁺/H₂ redox potential and 1.090 eV below the H₂O/O₂ redox potential, respectively. Similar behaviour is observed for KTO where the conduction and valence band potentials obtained from TB09 functional are located -1.356 eV above the H⁺/H₂ redox potential and 1.674 eV below the H₂O/O₂ redox potential, respectively. Owing to its superior performance in determining the electronic structures of perovskites, it is clear from Fig. 6 that the band edge potentials of both

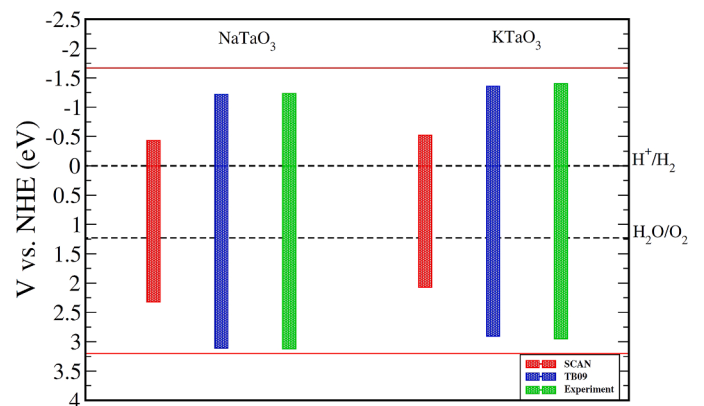


Fig. 6. The calculated band edge potentials for NaTaO₃ and KTaO₃ computed using the SCAN (red bars) and TB09 (blue bars) meta-GGAs. The experimental band gaps from Refs. [49,75] are used for computing their corresponding band edge potentials (green bars).

conduction and valence bands computed using the TB09 meta-GGA are in accord with experimental band edge potentials.

4. Conclusions

In summary, we have performed first-principles calculations to investigate the physical properties of alkali-metal tantalates ATaO_3 ($\text{A}=\text{Na}$ and K). The structure, stability, electronic, optical, and photocatalytic properties of NaTaO_3 and KTaO_3 are examined by employing meta-GGA functionals of DFT. For an accurate determination of the physical properties of tantalates, we model the exchange-correlation effects by systematically combining the SCAN and TB09 meta-GGAs. The structure and stability of orthorhombic and cubic phases of NaTaO_3 and KTaO_3 , respectively, are computed using the SCAN meta-GGA in terms of enthalpy of formation, reaction energies, elastic constants and phonon frequencies. On the other hand, to examine the electronic, optical and photocatalytic properties of these perovskites both SCAN and TB09 meta-GGAs are used for computing the electronic density of states, band structures, optical absorption and band edge potentials of conduction and valence band edges. Our results clearly indicate that the SCAN meta-GGA functional can accurately predict the experimentally observed structural, energetic, mechanical and dynamical properties for alkali-metal tantalates. Especially, the computed structural and energetic properties for elemental solids, binary and ternary oxides show that SCAN meta-GGA functional performs better than semi-local and is comparable to hybrid functionals. The calculated Young's modulus for NTO and KTO confirm the qualitatively equal stiffness of the two systems. On the other hand, having Poisson's ratio less than 0.25 indicates that both these materials are brittle and predominantly covalent in their bonding characteristics. We show that inclusion of SOC interactions is necessary for obtaining correct band dispersions and electronic properties of NaTaO_3 and KTaO_3 . On the other hand, the TB09 with the inclusion of SOC show that NTO has a direct band gap of 4.328 eV while KTO has an indirect fundamental band gap of 3.580 eV which can only be achieved through computationally expansive GW calculations. In accordance with available experimental data, only TB09 functional confirms that both NTO and KTO are active in the UV region of the electromagnetic spectrum. Moreover, using the electronic properties calculated with TB09 potential functional we have obtained reliable absorption coefficients the band edge potentials for NTO and KTO which indicates that these materials are potential candidates for photocatalytic water splitting. The outcomes of the present study can provide useful guidelines for accurately modeling the modulations in the physical properties of these materials using supercell approach for evaluating the influence of dopants or surface properties that are generally inaccessible with computationally demanding hybrid-DFT or GW calculations.

Data statement

The data that support the findings of this study will be made available upon reasonable request.

CRediT authorship contribution statement

Farrukh Javed: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Waqas Zulfiqar:** Writing – original draft, Data curation, Conceptualization. **Sirag Ahmed:** Methodology, Investigation, Formal analysis. **Ghulam Abbas:** Writing – review & editing, Validation, Formal analysis. **Syed Muhammad Alay-e-Abbas:** Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful to the Higher Education Commission of Pakistan for financial support under the National Research Program for Universities Grant No. 7107/Punjab/NRPU/R&D/HEC/2017. F. J. thanks the Higher Education Commission of Pakistan for the award of an International Research Support Initiative Program (IRSIP) scholarship. The computations were enabled by resources provided by Computational Materials Modeling Laboratory, Government College University, Faisalabad.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.materresbull.2024.113252](https://doi.org/10.1016/j.materresbull.2024.113252).

Data availability

Data will be made available on request.

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