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# Computational study of half-metallic behavior, optoelectronic and thermoelectric properties of new $XAlN_3$ (X = K, rb, cs) perovskite materials

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## Abstract

In this study, we systematically explored the properties of novel perovskite materials, $XAlN_3$ (X = K, Rb, and Cs), based on first-principles calculations and semiclassical Boltzmann transport theory. Generalized gradient approximation and HSE06 hybrid functional methods were used to investigate the electronic band structures. Our findings indicated intriguing half-metallic behavior where the spin-down state had metallic characteristics, whereas the spin-up state behaved as an insulator for all compounds, with indirect band gaps. These compounds had a significant magnetic moment of 5 $\mu_B$, which confirmed their half-metallic nature. Analysis of the elastic constants indicated distinctive mechanical properties. Moreover, the dielectric functions indicated efficient energy absorption across a broad energy spectrum, which is particularly beneficial for ultraviolet optoelectronic applications. At 300 K with a chemical potential ($\mu$) of +1.37 eV, $CsAlN_3$ had a notable thermoelectric figure of merit (ZT) of 0.99. This ZT value remained competitive at 0.97, even at a high temperature of 1000 K in the p-type region. However, the ZT and Seebeck coefficients decreased in a temperature-dependent manner to affect the thermoelectric characteristics of these materials. Overall, our findings suggest that $XAlN_3$ (X = K, Rb, and Cs) perovskite materials are promising candidates for use in various applications in spintronics, optoelectronics, and thermoelectric devices.

## Introduction

The perovskite structure represented by the chemical formula $ABX_3$ is important in materials science and condensed matter physics. This widely studied structure consists of two distinct cations (A and B) bonded to an anion (X) and it is often visualized as a cubic configuration with B atoms at the center surrounded by an octahedral arrangement of anions. Perovskite materials have great potential for use in various applications, including photovoltaics, light-emitting devices, sensors, and memory devices. Their high efficiency, low cost, and simple fabrication make them attractive for applications in renewable energy technologies [[1], [2], [3], [4], [5]]. Perovskites also have unique optical and electronic properties, which make them promising for uses in next-generation electronic devices [[6], [7], [8]]. Researchers have focused on ordered perovskite compounds, particularly because of their potential uses as magnetic electrodes. For example, Rubal et al. developed new perovskite materials and proposed that their properties have many potential applications [[9], [10], [11], [12], [13]]. Perovskite structures are of significant interest in spintronics, where electron

spin is harnessed for information processing. In 1983, De Groot et al. [14] conducted first-principles calculations to show that perovskites can achieve 100% spin polarization at the Fermi level. These half-metallic ferromagnetic materials possess unique electronic structures, where one spin channel behaves metallically driven by the majority of the metallic spin electrons whereas the other exhibits semiconducting or insulating characteristics to result in 100% spin polarization at the Fermi level. These materials have advantages, such as reduced energy consumption, higher circuit integration density, and faster data processing, thereby placing them at the forefront for applications in advanced electronics [15].

Theoretical studies by Mir et al. predicted the dynamic stability and half-metallic characteristics of $BaMO_3$ (M = Mg and Ca) perovskites [16]. In 2022, Abdullah et al. determined the stability and half-metallic properties of titanium-based fluoro-perovskite $MTiF_3$, where M represents Rb and Cs. These materials exhibit metallic properties in the spin-up state and nonmetallic properties with a large indirect band gap in the spin-down state [17]. Cai et al. investigated the perovskite $BiNiO_3$ and demonstrated its half-metallic ferromagnetism due to strong p-d exchange interactions, thereby resulting in semiconducting behavior in the majority-spin electrons and metallic behavior in the minority-spin electrons [18]. Abdullah et al. demonstrated the potential uses of double perovskites $K_2NaMI_6$ and $K_2NaMCl_6$ (M: Cr, Fe), as well as $Cs_2GeSnX_6$ (X = Cl, Br, I) for thermoelectric and spintronic applications because of their interesting optical and thermoelectric properties, with useful applications in semiconductor and optoelectronics industries [[19], [20], [21]]. Rahman et al. identified promising materials including halide and oxide perovskites, as well as novel inorganic cubic perovskites, for applications in solar cells, optoelectronic devices, and gas sensors [11,[22], [23], [24]]. These insights into perovskite materials have contributed to their exploration and utilization in a range of technological applications.

The scientific community must address two pressing energy-related challenges comprising the ongoing energy crisis and growing environmental concerns related to conventional energy sources. Perovskite materials may provide promising solutions, particularly in thermoelectric applications [25]. The efficiency of thermoelectric materials is quantified by the dimensionless figure of merit (ZT): $ZT = S^2\sigma T/\kappa$, where S represents the Seebeck coefficient, σ denotes the electrical conductivity, T indicates the temperature, and κ is the thermal conductivity [[26], [27], [28], [29], [30]]. Researchers have aimed to develop thermoelectric materials with high Seebeck coefficients, strong electrical conductivity, and low thermal conductivity to maximize the ZT values. Recent studies based on density functional theory have elucidated the thermoelectric potential of perovskite materials. In particular, $RbNpO_3$ and $RbPuO_3$ were found to have ZT values of 1.01 and 0.987 at 300 K, respectively, thereby indicating their suitability for use in both low- and high-temperature thermoelectric devices [31]. In addition, studies have identified $CaMnO_3$, $SrTiO_3$, and $BaTiO_3$ as promising alternatives to traditional thermoelectric materials, although chalcogenide thermoelectric materials currently achieve the highest ZT values [27].

Only a limited number of new nitride perovskites with potential applications have been theoretically predicted and synthesized. $ThTaN_3$ is an important example that demonstrates the potential of nitride perovskites because it has characteristics similar to those of a topological crystalline insulator [32]. Another notable nitride perovskite, $LaWN_3$, was theoretically predicted and synthesized, and it exhibited impressive ferroelectric properties. However, its application in optoelectronics is hindered due to its status as an indirect-gap semiconductor [33]. Recently, Viet-Anh et al. identified as $CeTaN_3$ and $CeNbN_3$ promising candidates, with direct semiconducting band gaps of 1.5 eV and 1.1 eV, respectively [34].

In the present study, we comprehensively investigated the structural parameters, electronic behaviors, mechanical stability, optical properties, and thermoelectric characteristics of $XAlN_3$ perovskites, where X represents K, Rb, or Cs. Our primary aim was to identify new half-metallic compounds with significant band gaps in the spin-up channels, with potential applications in the field of spintronics. We also investigated how these band gap variations might impact the optical properties and thermoelectric efficiency. Thus, based on computational predictions, we obtained valuable insights into the half-metallic and thermoelectric properties of these nitride perovskites. These findings are important for advancing both spintronic and thermoelectric devices.

## Section snippets

## Computational methods

We performed first-principles calculations using the CASTEP simulation code [35] with the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof exchange-correlation potential [36]. Ultrasoft pseudopotentials were employed to enhance the computational efficiency but without sacrificing accuracy [37]. The energy cutoff was 500 eV for the plane-wave basis set, and we utilized 10 × 10 × 10 k-points for geometry optimization, whereas the electronic, magnetic, elastic, optical, and…

## Structural and electronic properties

The perovskite materials $XAlN_3$ (X = K, Rb, Cs) are aluminum-based nitro-perovskites with a cubic phase and pm3m space group (no. 221). The Wyckoff coordinates of the atoms in this phase are X located at (0, 0, 0), whereas Al and N atoms are located at (0.5, 0.5, 0.5) and (0, 0.5, 0.5), respectively, as shown in Fig. 1. First, we performed structural optimization and the equilibrium lattice constants obtained for these three perovskite compounds are listed in Table 1. To further confirm the…

## Conclusion

In this study, we investigated new perovskite materials with the cubic phase $XAlN_3$ (X = K, Rb, and Cs). The structures were optimized and shown to be thermodynamically stable based on the formation energy, where $RbAlN_3$ was the most stable compound. The GGA method was utilized to analyze the electronic band structures of the materials and to elucidate their insulating properties. We also used the HSE06 hybrid functional due to its more accurate calculation of the band gap, and the results…

## CRediT authorship contribution statement

**Ahmed H. Ati:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Ammar A. Kadhim:** Writing – review & editing, Software, Investigation, Conceptualization. **Ali A. Abdulhussain:** Software, Resources, Investigation. **Wed A. Abed:** Software. **Kadhim Fadhil Kadhim:** Software. **Maged Abdullah Nattiq:** Software.…

## Declaration of competing interest

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