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INFLUENCE OF SUBSTITUTION WITH STRONTIUM ATOMS ON THE ELECTRONIC PROPERTIES OF $K_{0.5}Bi_{0.5}TiO_3$, AS STUDIED BY MEANS OF AB INITIO METHODS*

Grzegorz Jagło[†], Piotr Czaja
Kamila Kluczewska-Chmielarz

Institute of Technical Sciences, University of the National Education Commission
Podchorążych 2, 30-084 Kraków, Poland

Jan Suchanicz

Department of Mechanical Engineering and Agrophysics
University of Agriculture in Kraków
Balicka 120, 31-120 Kraków, Poland

Dorota Sitko

Faculty of Exact and Natural Sciences
University of the National Education Commission
Podchorążych 2, 30-084 Kraków, Poland

Danuta Goc-Jagło

Institute of Theoretical Physics, Jagiellonian University
Łojasiewicza 11, 30-348 Kraków, Poland

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First-principles density functional calculations were performed to calculate the physical properties of the lead-free $K_{0.5}Bi_{0.5}TiO_3$ and $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ ferroelectric systems. In particular, the A-site cation ordering in $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ and its influence on the density of electronic states were explored. The results suggest that cation ordering at A sites in $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ significantly affects its density of electronic states spectra. The density of electronic states and the band structure of states for these systems were computed to determine the differences in spectra shape with respect to the band gap. It was found that in $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$, the band gap is larger than for the $K_{0.5}Bi_{0.5}TiO_3$ system by 0.2 eV. The density

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[†] Corresponding author: `grzegorz.jaglo@uken.krakow.pl`

of electronic states and band structure spectra are required to provide reference first-principles data for further theoretical considerations and analysis of experimental spectra. The proposed calculations will also be used in the subsequent search for materials optimal for application in photovoltaics.

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1. Introduction

The structure and physical properties of perovskites make them highly promising materials from the perspective of a variety of technological applications. The development of new perovskite materials such as the bismuth-containing $\mathrm{Na_{0.5}Bi_{0.5}TiO_3}$ (NBT) and $\mathrm{K_{0.5}Bi_{0.5}TiO_3}$ (KBT) has made it possible to search for efficient lead-free piezoceramic materials that might serve as alternatives to the environmentally hazardous $\mathrm{Pb(Zr,Ti)O_3}$ (PZT) [1–6]. This also applies to certain solid solutions, for example, KBT-$\mathrm{SrTiO_3}$ (KBT-STO). At room temperature, $\mathrm{K_{0.5}Bi_{0.5}TiO_3}$ crystallizes in the tetragonal space group P4mm. The reported experimental lattice parameters for tetragonal $\mathrm{K_{0.5}Bi_{0.5}TiO_3}$ are $a = b = 3.913$ Å and $c = 3.990$ Å [7, 8]. At $T_{\mathrm{C}} \sim 370$–410°C, the structure of KBT changes from paraelectric cubic $Pm\bar{3}m$ to pseudocubic, and at $\sim$ 270–310°C a transition to ferroelectric tetragonal P4mm is observed [9].

The aim of the presented study was to analyze whether methods such as *ab initio* can be used for calculations performed to evaluate the features of perovskite-like oxide compounds. Some K atoms in the $\mathrm{K_{0.5}Bi_{0.5}TiO_3}$ base material were substituted with strontium atoms, and its electronic structure was then studied to determine the effect of this modification. The present research was undertaken as part of a program aimed at modifying KBT to expand its range of potential applications, which include photovoltaics. It is expected that theoretical calculations will allow for the selection of admixtures that are optimal in terms of both the applied elements and the specific amounts used for doping.

2. Methodology

Calculations were performed without incorporating the spin-polarized density functional theory, using the PWscf code implemented in the QUANTUM ESPRESSO package [10]. Electron–ion interactions were represented by pseudopotentials as part of the projector-augmented wave (PAW) scheme. The valence electron configurations of the data set were as follows: K $3p^6 4s^1$, Bi $5d^{10} 6s^2 6p^3$, Ti $3s^2 3p^6 4s^2 3d^2$, O $2s^2 2p^4$, and Sr $3d^{10} 4s^2 4p^6 5s^2$. The exchange-correlation potentials were handled by applying the Perdew–Burke–Ernzerhof (PBE) [11] form of generalized gradient approximation (GGA). Such functionals are sufficiently accurate for the description of the electronic properties of perovskite systems [12–15].

For KBT and the $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ solid solution, an ordered supercell $2 \times 2 \times 2$ with 40 atoms in the tetragonal cell was constructed, as shown in Fig. 1. The computations were performed for one of the many possible $K_{0.5}Bi_{0.5}TiO_3$ ion placements by substituting two K ions with two Sr ones. This system roughly simulates the structure of $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$. The sampling of Brillouin zones of $2 \times 2 \times 2$ (40 atoms) $K_{0.5}Bi_{0.5}TiO_3$ unit cells was performed using $4 \times 4 \times 4$ Monkhorst–Pack k-point meshes. Both structures were completely relaxed with a mesh of $4 \times 4 \times 4$. While calculating the projected density of states (PDOS), the k-space mesh was likewise $4 \times 4 \times 4$. In the computations, a plane-wave basis with a kinetic energy cutoff of 650 Ry was used. The values of total energy were approximated to 10^{-4} eV/cell to achieve self-consistency in the calculations.

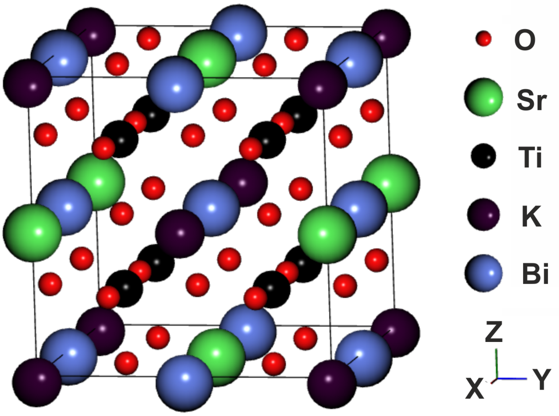

Fig. 1. 111 configurations of the applied $2 \times 2 \times 2$ perovskite supercell of $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ with a tetragonal lattice.

3. Results and discussion

Figure 2 shows the calculated total and partial densities of electronic states for $K_{0.5}Bi_{0.5}TiO_3$. The conduction band (CB) in the range of 1.8–6.2 eV consisted mainly of the Ti (3d) orbitals and, to a lesser extent, of the Bi (6p) states. For comparison, in article [16], this range was calculated at 2.0–5.8 eV. The dominant contribution at the top of the conduction band originated from the Ti (3d) electrons. The highest hybridization in the CB was observed in the middle region of the band formed by the Ti (3d) and

Bi (6*p*) states. The valence band (VB) is wider than the conduction band (CB) and was calculated to be 5.6 eV. The valence band consisted mostly of O (2*p*) states. Hybridization also occurred in the lower-energy section of the VB and originates from the O (2*p*) and Bi (6*p*) orbitals, however, it was much weaker than in the case of the CB.

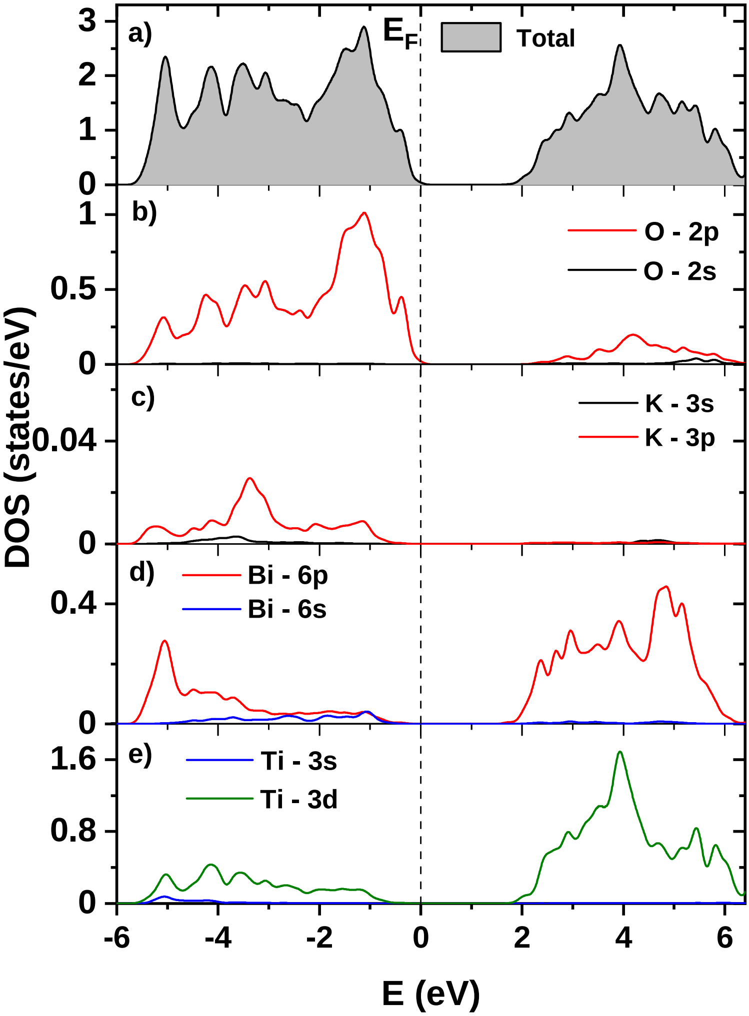

Fig. 2. (a) Total density of states in $K_{0.5}Bi_{0.5}TiO_3$. Partial density of states in $K_{0.5}Bi_{0.5}TiO_3$ projected onto orbitals of (b) O atom, (c) K atom, (d) Bi atom, and (e) Ti atom. The top of the valence band (VB) is indicated by the dashed line at 0 eV.

The calculations showed that in the Sr-doped compound, both the valence and conduction bands grew wider (Fig. 3). The influence of the components forming the VB and CB bands was similar to what was observed for KBT. As in the case of KBT, the contribution from K orbitals was negligible. The contribution from Sr orbitals was small. Greater hybridization in the conduction band determined by Ti ($3d$) and Bi ($6p$) states was observed, especially in the lower-energy region of the band.

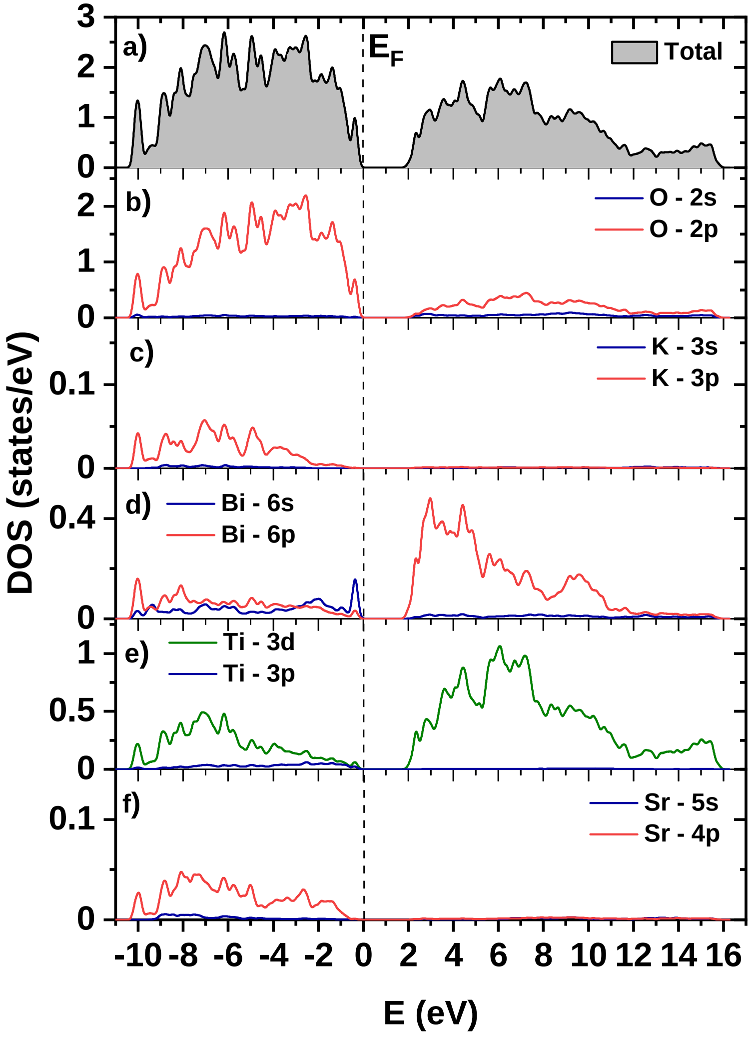

Fig. 3. (a) Total density of states in $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$. Partial density of states in $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ projected onto orbitals of (b) O atom, (c) K atom, (d) Bi atom, (e) Ti atom, and (f) Sr atom. The top of the valence band (VB) is indicated by the dashed line at 0 eV.

The results shown in Fig. 4 confirm that the valence band was formed mainly by oxygen atoms, while the conduction band was determined by the Bi and Ti atoms for both $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ and KBT. Moreover, the contributions from the valence states of K to the occupied bands were relatively small, since the potassium atoms present in the crystal occurred in the K^+ ionic state.

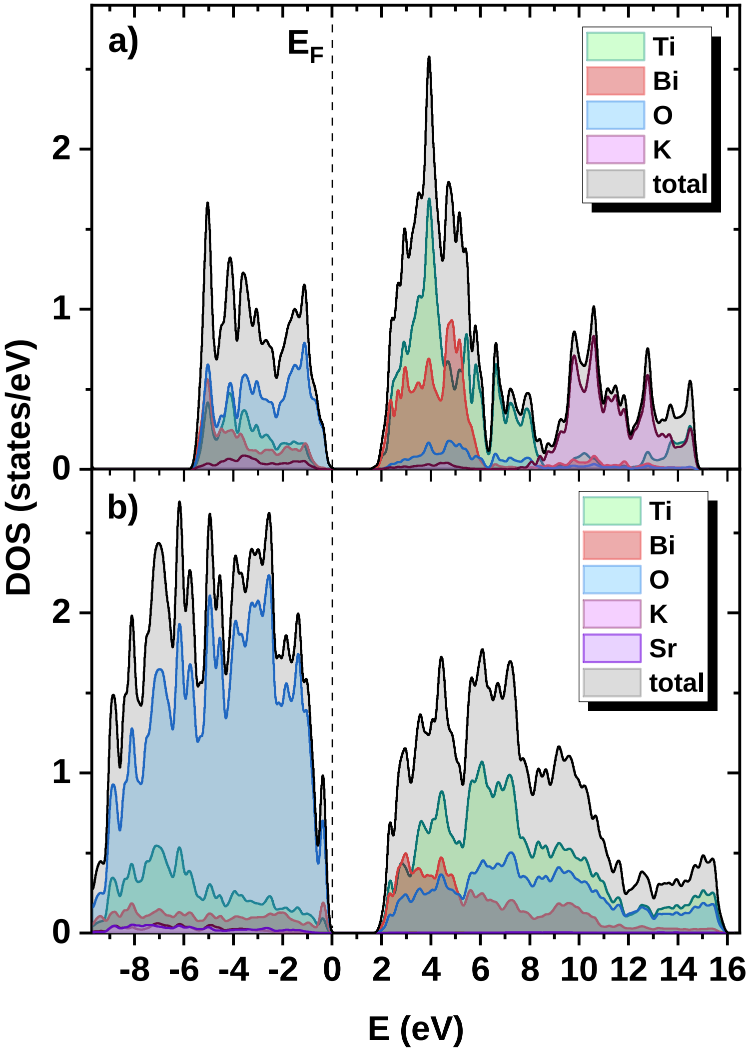

Fig. 4. Total and partial density of states in: (a) $K_{0.5}Bi_{0.5}TiO_3$ and (b) $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$.

The calculated band structures of $K_{0.5}Bi_{0.5}TiO_3$ and $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ compounds are compared in Fig. 5 and Fig. 6. The calculated band gaps at the Γ-point were 1.8 and 2.05 eV for KBT and $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$, respectively. This difference in band-gap values between the valence and conductivity bands was due to differences in the cation atoms and the crystal structure of these two systems, which was a consequence of the substitution of two potassium ions with two strontium atoms. Potassium has an unfilled *s* subshell, whereas all *s* subshells of strontium are full.

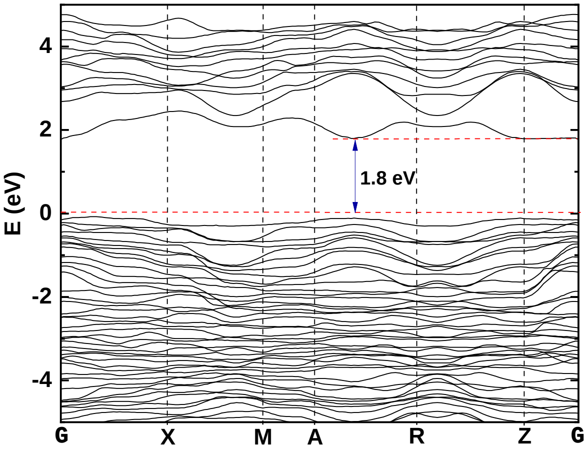

Fig. 5. Computed (GGA) energy band structure of $K_{0.5}Bi_{0.5}TiO_3$ along the high-symmetry directions in the Brillouin zone.

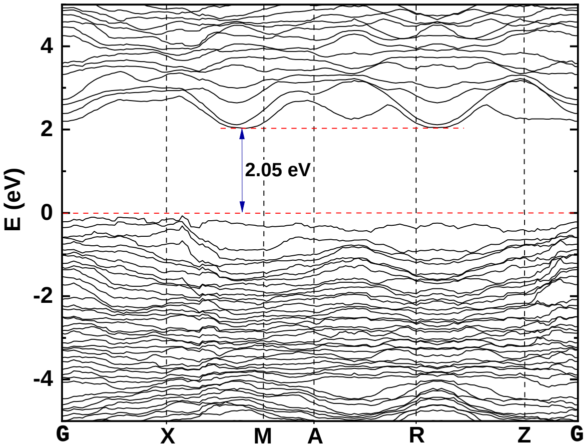

Fig. 6. Computed (GGA) energy band structure of $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ along the high-symmetry directions in the Brillouin zone.

The calculated E_{Tot} values were -11101.21 and -11595.31 eV for KBT and $K_{0.25}Sr_{0.25}$ E_{Tot}, respectively (see Table 1).

Table 1. Parameter values calculated for $K_{0.5}Bi_{0.5}TiO_3$ and $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ [eV].

	$K_{0.5}Bi_{0.5}TiO_3$	$K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$
Tot. energy	-11101.21	-11595.31
Calc. gap	1.8	2.05
Exp. gap	3.31 [17]	3.25–3.75 [18]

4. Summary and conclusions

In this work, calculations based on the density functional theory (DFT) were performed to study the density of electronic states in $K_{0.5}Bi_{0.5}TiO_3$ after doping with the strontium atoms. The electronic structures of KBT and $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ were computed using the QUANTUM ESPRESSO code in the framework of DFT. The calculation of DFT was carried out using GGA, with PBE parametrization and without taking into account spin polarization. It was determined that the band gap for $K_{0.25}Sr_{0.25}Bi_{0.5}TiO_3$ is larger than for KBT by 0.2 eV. The increase in the energy gap is influenced by the fact that all strontium *s* subshells are full, while potassium has an unfilled *s* subshell. This result can be explained by the fact that the experimental energy gap in $SrTiO_3$ (STO) is 3.25–3.75 eV [18], which is greater than in the case of KBT. It can, therefore, be concluded that doping KBT with Sr atoms leads to an increase in the band gap. For KBT, this value is consistent with the experimental value of 3.31 eV [17]. It should be noted that calculations performed so far with various *ab initio* codes and methods indicate that the optical gap ranges from 2.31 to 3.96 eV [19] for STO.

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