Electronic properties and X-ray absorption spectra of Ba$_{1-x}$K$_x$BiO$_3$

Yaroslav Zhumagulov$^{1,2}$, Andrey Krasavin$^1$, Alexander Lukyanov$^1$, Vyacheslav Neverov$^1$, Alexander Yaroslavtsev$^{1,3}$ and Alexey Menushenkov$^1$

$^1$National Research Nuclear University MEPhI, 115409 Moscow, Russian Federation
$^2$ITMO University, 197101 Saint Petersburg, Russian Federation
$^3$European XFEL GmbH, 22869 Schönefeld, Germany

E-mail: slavesta10@gmail.com

Abstract. The band structure, the density of states, and X-ray absorption spectra of the oxygen K-edge for perovskite high-temperature superconductors based on BaBiO$_3$ are calculated by the density functional theory method for different levels of potassium doping in the ground and optically excited states. It is shown that changes in the properties of the electronic subsystem near the Fermi level can be correctly described by taking into account local structural inhomogeneities caused by doping and exposure to optical radiation. The appearance with doping of hole carriers on the hybridized Bi6s – O2p$_{\sigma}$ orbital is demonstrated, which agrees with the model of the electronic structure of bismuthate high-temperature superconductors based on a spatially separated Fermi-Bose mixture.

1. Introduction

Despite the enormous number of experimental and theoretical studies carried out over more than 30 years after the discovery of high-temperature superconductivity (HTSC) in cuprates, the universally accepted view of the origin of HTSC has not yet been developed. Therefore, the use of new experimental methods becomes decisive for explaining the mechanism of HTSC. Studies of nonequilibrium processes in pump-probe experiments, which can be implemented with the advent of X-ray free electron lasers, provide new unique information about the fast dynamics of the electronic and lattice properties of high-temperature superconductors (HTSCs) [1–5]. Related to cuprates, the family of superconducting oxides is represented by perovskite-like superconductors based on BaBiO$_3$. Cubic superconducting oxides BaPb$_{1-x}$Bi$_x$O$_3$ (BPBO) and Ba$_{1-x}$K$_x$BiO$_3$ (BKBO) have been widely studied since 1975 [6] and 1988 [7], respectively. To explain HTSC in these compounds, numerous ab initio calculations have been carried out; however, most of the unusual properties of BaBiO$_3$-based compounds described in an early review by Uchida et al. [8] remain unexplained. Unlike layered cuprates, bismuth compounds crystallize into a three-dimensional cubic structure; the parent bismuthate compound BaBiO$_3$ is characterized by charge ordering and charge density wave (CDW). Therefore, the magnetic mechanism is excluded from possible explanations of the nature of HTSC in bismuthates. Due to the significantly greater Bi-O bond length of octahedral complexes in BaBiO$_3$ (2.4 Å) compared to the Cu-O bond length in cuprates (1.9 Å), bismuthates have significant advantages for studying by locally sensitive methods such as EXAFS and XANES. Recently, low-temperature EXAFS studies of BKBO and BPBO compounds [9, 10] showed the presence of anomalous lattice vibrations associated with the motion of local electron pairs. It was found that
different electron filling of the upper antibonding Bi6s – O2pν orbital of neighboring octahedral BiO6 complexes leads to the formation of a double-well potential in which oxygen ions oscillate. As was shown in [9, 10], a large soft octahedron is a BiO6 complex with an electron pair, and a smaller rigid octahedron is a BiL2O6 complex with a hole pair on the upper antibonding Bi6s – O2pν orbital (here L2 denotes the free level in the antibonding orbital). The double-well potential of oscillations of oxygen ions arises due to the tunneling of a local electron pair between adjacent octahedra in accordance with the dynamic exchange. In an experiment, BaBiO3 demonstrates a semiconductor behavior with an activation gap $E_a = 0.24$ eV, which can be explained only as a two-particle transfer with an activation energy of $2E_a$ due to the delocalization of local pairs [10].

It is important to note that the presence of local inhomogeneities in the form of oscillations of ions in a double-well potential is also a common characteristic feature of other HTSCs, including cuprates [11–14] and iron-based HTSCs [15, 16].

Recently, a new description of the local electronic structure in BaBiO3 was proposed in [17] which is based on the existence of a spatially separated Fermi-Bose mixture. It was shown that two types of charge carriers, local electron pairs (bosons) and free electrons, coexist in metallic BKBO with $x \geq 0.37$. Bosons are responsible both for charge transfer in the parent BaBiO3 semiconductor and for superconductivity in metallic BKBO, and the fermionic subsystem induces the observed metal–dielectric phase transition and the appearance of a Fermi-liquid state upon overcoming the percolation threshold. Bosons and fermions occupy different types of octahedral complexes BiO6, and are always separated in real space. Therefore, the ground state of BaBiO3 is a new quantum state of a pair-charge-density wave (PDW). This interpretation of the ground state is fundamentally different from an ordinary CDW traditionally utilized in the literature (see, for example, [18] and references therein). There are no free electrons in BaBiO3, and the conductivity can only be due to the movement of local electron pairs. This possibility was first qualitatively formulated in the bipolaron language by Uchida et al. [8], and then theoretically confirmed by Taraphder et al. [19].

Our understanding of the excitation processes in oxides based on BaBiO3 is very different from that proposed in [18]. From our point of view, the PDW gap differs from the CDW gap because of the existence of spatial separation of local pairs of electrons and holes on BiO6 and BiL2O6 octahedra, respectively. We assume that laser excitation through the optical gap should lead to the destruction of a local pair when a single electron from a BiO6 octahedron transfers to the adjacent BiL2O6 octahedron. As a result, another electronic structure appears in the form of two identical BiL2O6 octahedra, which should lead to a strong local lattice distortion. In addition, a local magnetic moment should appear on BiL2O6 octahedra. Experimental confirmation of the model in Ref. 17 can be obtained by the methods of X-ray absorption spectroscopy with time resolution on an X-ray free electron laser with femtosecond optical excitation through the PDW gap.

The purpose of this work is the preliminary study of the dynamical local distortion of the crystal lattice arising from femtosecond optical excitation by ab initio calculations of the band structure, the density of states, and XAS spectra of the parent and doped systems based on BaBiO3. It is shown that the phenomenological model in Ref. 17 based on the observation of the double-well potential of oxygen ion oscillations and the existence of two different states of bismuth makes it possible to correctly describe the electronic properties of high-temperature BaBiO3-based superconductors both in the ground and optically excited states. The theoretical description of BaBiO3-based compounds in the framework of the density functional theory (DFT) is possible because electrons occupying Bi6s and O2p orbitals in BaBiO3 are weakly correlated [18].

2. Method

The electronic structure was calculated within the framework of the density functional theory using the full potential method of linearized augmented plane waves (FP-LAPW) implemented in the Wien2k software package [20]; to take into account the exchange correlation potential, the PBE gradient correction [21, 22] was used with a resolution of 400 $k$-points in the first Brillouin zone.
The crystal structure of the ground state in the undoped regime was taken from [23] (figure 1a). The structure is characterized by a distortion of the ideal cubic perovskite lattice; the BiO$_6$ octahedra are tilted at the angle of 11° and have a different size determined by the filling of the antibonding orbital. Large and soft octahedra BiO$_6$ alternate with rigid BiL$_2$O$_6$ octahedra of smaller size having a hole pair on an antibonding orbital.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Schematic representation of the crystal structure of Ba$_{1-x}$K$_x$BiO$_3$: a) ground state, $x = 0$; b) excited state, $x = 0$; c) ground state, $x = 0.5$; d) excited state, $x = 0.5$. Bismuth atoms are shown yellow in L$_2$ octahedra, blue in BiO$_6$, and green in L$_1$ octahedra; oxygen atoms and octahedron boundaries are shown in red; atoms of barium and potassium in white and pink, respectively.

Doping the system with potassium leads to the appearance of additional hole carriers, which is accompanied by the steady replacement of large BiO$_6$ octahedra by small BiL$_2$O$_6$ ones [10], as well as by decreasing the perovskite lattice distortion and the lattice parameter [24]. At concentrations $x \geq 0.37$, a structure emerges that integral experimental methods (neutron diffraction) see as simple cubic [24], and EXAFS indicates the presence of the double-well potential where different octahedra BiO$_6$ and BiL$_2$O$_6$ adjoin, and the harmonic potential between identical BiL$_2$O$_6$ octahedra [10]. In this work, the doping degree $x = 0.5$ was chosen based on considerations of simplicity of modeling (the unit cell in this case is only doubled), as well as to eliminate possible effects associated with the uneven distribution of potassium and barium in the crystal lattice. With this degree of doping, the lattice has a regular structure of octahedra with a size of 2.20 Å; the antibonding orbital remains filled on each fourth octahedron (figure 1c). To simulate this structure, local changes $\Delta$ of the charge on bismuth atoms were introduced into the regular crystal lattice, which resulted in the necessary redistribution of the electron density; the value $\Delta = 0.43$ was chosen in accordance with the change in the filling of the Bi6s orbital calculated in [25].
The excited state of the undoped system is formed under the influence of laser radiation with energy of about 2 eV: the hole pair on the octahedron breaks apart, and instead of different BiL₂O₆ and BiO₆ octahedra, two identical BiL₂O₆ octahedra are formed with the size equal to the half-sum of the sizes of the original octahedra in the first approximation. The distortions of the cubic lattice disappear (figure 1b). The effect of laser radiation on the doped system occurs in a similar way, but in this case there are half as many hole pairs on the antibonding orbital (figure 1d); the simulation of this structure was carried out by introducing an additional charge Δ/2 to bismuth atoms in L₁ octahedra. X-ray absorption spectra were calculated using the core-hole technique [26] with [2×2×2] supercell to minimize the interaction of the excited atom with its periodic images.

3. Results
Figure 2 shows the band structure and partial densities of atomic states that make the main contribution to the band structure near the Fermi level. The ground state of the undoped compound is an insulator with the transport gap of about 0.3 eV, in good agreement with the result $E_a = 0.24$ eV obtained in [8]. When the undoped system is excited, a crystal structure emerges in which atoms of each type form a simple cubic lattice, and an insulator – metal phase transition is observed. Since the main contribution to the density of states near the Fermi level is determined by oxygen atoms that also form a simple cubic lattice, the band structure near the Fermi level becomes equivalent to the band structure of the tight-binding model of the cubic lattice with nearest-neighbor hoppings (figure 2b). The excitation of the doped system also significantly changes the band structure near the Fermi level, while the partial densities of states of bismuth and oxygen stay almost unchanged; the system remains metallic.

Figure 3 shows the XAS spectra of the oxygen K-edge for all the systems under consideration. The main result is the evolution of the spectra of the ground state with the change of doping. When the system is doped, only a certain redistribution of intensity occurs; the left peak shifts towards lower energies and the metallic behavior of the system, and the intensity of the two main peaks remains almost unchanged. This behavior is in complete agreement with the results of precision measurements carried out in [27], and suggests that at doping hole carriers appear on the hybridized Bi₆s – O₂pₐ orbital, or otherwise on the spectrum of BKBO in figure 3 either an additional pre-peak would arise, or the amplitude of the first BKBO peak would be substantially larger than the amplitude of the first BaBiO₃ peak.

It is impossible to obtain correct XAS spectra of the bismuth N-edge within the framework of the density functional theory, since f-electrons are strongly correlated, and other methods are needed to correctly take into account correlations, such as, for example, methods based on solving the tight-binding model for Ba₁₋ₓKₓBiO₃: the variational cluster approximation [28, 29]) or the dynamical mean field theory [30].

4. Conclusions
Using ab initio calculations, we obtained the density of states, the band structure, and X-ray absorption spectra for perovskite HTSCs based on BaBiO₃ in the ground and optically excited states; $x = 0$ and $x = 0.5$ degrees of doping were considered. The corresponding changes in the properties of the electron subsystem near the Fermi level were correctly described by taking into account local structural inhomogeneities of the crystal lattice. It was shown that upon doping, hole carriers appear on the hybridized Bi₆s – O₂pₐ orbital, which is in agreement with the phenomenological model of the electronic structure of bismuthate HTSCs based on a spatially separated Fermi-Bose mixture [17]. Considering that the manifestation of local structural inhomogeneities in the form of ionic oscillations in a double-well potential is a common property of high-temperature superconductors including cuprates and iron-based HTSCs, the proposed approach may be useful for describing the ground and excited states in other high-temperature superconductors.
Figure 2. The band structure (in the middle) and the partial densities of the oxygen (left) and bismuth (right) states near the Fermi level for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$: a) ground state, $x = 0$; b) excited state, $x = 0$. When calculating the density of states, the Gaussian blur parameter was taken equal to 0.03.

Figure 3. X-ray absorption spectra of the oxygen $K$-edge for the ground state for undoped and doped compounds.
Acknowledgments
The work was supported by Russian Found for Basic Research (project No.18-02-40001 mega).

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