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Properties of $BiMnO_3$ and $BiMn_{0.5}Nb_{0.5}O_3$ from ab initio simulations

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HIGHLIGHTS

- DOS for defected BMO, BMNO crystals have been presented.
- The exchange energy is on the level about 23% of the total energy.
- The gap energy achieved values in the range $E_g = 0.2 - 0.5$ eV for BMO and BMNO.

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ABSTRACT

Ab initio studies of structural and electronic properties of the monoclinic perovskite-type $BiMnO_3$ and $BiMn_{0.5}Nb_{0.5}O_3$ crystals are presented using the pseudo-potential plane wave method within the density functional theory in generalized – gradient approximation. The calculated equilibrium lattice parameters remain in a good agreement with the available experimental data. The gap energy took values in the range $E_g = 0.2 - 0.5$ eV for both compounds.

1. Introduction

First-principles modeling approaches are promising methods in studies of new materials. Particularly, these methods allow to study the influence of defects on electronic, structural and elastic properties of a chosen compound. Therefore, thanks to theoretical results one can predict in which manner the base materials should be modified in order to fit preferred physical properties of crystals [1]. Moreover, the production of new materials can be performed at lower cost while it is supported on the results related to the addition of atoms and controlled defects, that have been tested previously by the *ab initio* calculations. These actions are environmentally friendly.

Modern wireless systems have passed in the last ten years to the microwave region of the frequency. With a view to applying the multilayer technology, the development of new low-temperature-cofired ceramics (LTCC) with a sintering temperature lower than the temperature of 1273 K becomes one of the major goals. $BiNbO_4$ (BNO) as microwave dielectric is suitable to be used in multilayered microwave devices. BNO is antiferroelectric at the room temperature, but becomes ferroelectric at 633 K and paraelectric at 843 K [2]. The BNO ceramics and ceramics based on them have a low sintering temperature and the orthorhombic structure (space group Pnma), and they are good candidates for LTCC ceramics [3–7]. The structure can be viewed as a pseudo-layered structure in which the layers of NbO_6 octahedra are separated along the *b*-axis by Bi atoms.

The investigation of the influence of structural defects on an electronic structure of bismuth manganite by a method of the *ab initio* calculations is worthwhile since the bismuth manganite attracts attention due to its multiferroic features [8,9]. One can notice that the good quality $BiMnO_3$ (BMO) polycrystalite and BMO crystal samples production needs an application of a high pressure [10–14]. The standard high temperature sintering carried out at ambient air is possible [15], however, the better results are obtained at the high-pressure conditions. Such results suggest that the internal stress which rise during the synthesis can be overcome with the applied high pressure. Probably, either oxygen vacancies or oxygen atoms in interstitial positions can occur due to the thermo-dynamical conditions of the synthesis of the BMO samples. BMO shows insulator properties below the temperature of 100 K. However, thermally activated semiconductor properties with a band gap of about 0.26 eV or 0.33 eV were also reported [16], [17]. It was shown that the electronic structure of the ceramic perovskite materials depends on the oxygen non-stoichiometry [18]. Even if such defects occurrence might be assumed as the technological side effect, they can reduce the stresses of the crystal lattice. Hence, one of the aims of this work was realization of the *ab initio* calculations for the oxygen-defected BMO-based compounds. The other way to overcome the

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internal stresses that allows omitting the necessity of the high-pressure application was the purposeful doping of the crystal lattice [13].

The former works carried out on the $BiMnO_3$ - $NaNbO_3$ (BMO-NNO) compounds [19,20] showed that structurally proper, one-phase ceramics were obtained by sintering carried out at ambient pressure air and the occurrence of minor phases was diminished. From the first principles calculations the density of states, values of an energy gap, theoretical lattice parameters of the monoclinic phase for the BMO at the 0 K were obtained, *e.g.* Ref. [21]. In recent years, theoretical explanation of electronic properties has been extensively performed in many papers with using different more and more complicated methods par example based on Heisenberg type Hamiltonian [22] where were taken into account ferromagnetic and antiferromagnetic interactions between the nearest and farther neighbours atoms or another one [23] by using the modified Becke - Johnson exchange functional within the density functional theory.

The new compounds which allow for manipulation of magnetization with an electric field at the room temperature are looked for many years. We would like to propose material, may be a multiferroic with high T_C, M_S and P and simultaneously a good candidate for LTCC ceramics. We suppose that another type of these materials probably might be a solid solution of the bismuth manganite and bismuth niobate. We expect that combination of the bismuth niobate and bismuth manganite will cause the presence of electrical and magnetic properties in the new BMO-BNO system and those ceramics will be more useful, from technical point of view, than the pure compounds. We have been chosen the perovskite like $BiMnO_3$ system where a half of number of Mn ions was replaced by Nb ions. We investigated the possible properties of $BiMn_{0.5}Nb_{0.5}O_3$ by using a method of calculations from first principles. In this paper the monoclinic phase of BMO and BMNO together with a spin polarization and the influence of point defects are discussed.

The paper is organized as follows: the method of simulations is described in Section 2. In Section 3 the results and discussion of the structural, elastic and electronic properties as the results of our calculations are presented. Finally, the conclusions and remarks are given in Section 4.

2. Calculus methods and experimental procedures

The electronic structure for the bismuth manganite based compounds was simulated, *i.e.* for $BiMnO_3$ (BMO) and $BiMn_{0.5}Nb_{0.5}O_3$ (BMNO) crystals. The BMNO can be considered as the material belonged to the bismuth manganite - niobate system [24,25]. The simulations were carried out for the stoichiometric compounds from chemical point of view. However, in order to deduce the influence of point defects related to oxygen, the subsequent simulations were also performed for the species containing oxygen and bismuth vacancies (V_O, V_{Bi}) and interstitial oxygen (O_I) defects.

The starting values of lattice parameters for the monoclinic phase of BMO crystal were taken from X-ray data as $a = 9.5317(7)$ (Å), $b = 5.6047(4)$ (Å), $c = 9.8492(7)$ (Å), $\alpha = \gamma = 90^\circ$, $\beta = 110.60(1)^\circ$ [16]. The same lattice parameters were used for BMNO as the hypothetical starting crystallographic data in the relaxation procedure.

2.1. Method of calculations

The calculations were performed within the density functional theory (DFT) [26] using a linear combination of atomic orbitals (LCAO) with the localized basis set in the form of spherical functions as implemented in SIESTA 3.0 program together with the spin polarization [27,28]. The generalized gradient approximation (GGA) [29] was used for exchange-correlation functional energy.

After several beginning tests we have chosen, as the best, due to a plane wave energy cutoff of 550 Ry and 4 × 4 × 4 Monkhorst-Pack grid. The analyzed unit cell contained 40 atoms. Such number of atoms allowed the introduction of point defects into the system with a level of defects concentration about 2.5%. Only valence electrons were considered while others were replaced by the effective norm-conserving Troullier-Martins pseudo-potentials with Perdew, Burke, and Ernzerhof parametrization [30] for atomic configurations: Bi: $6s^2\ 6p^3\ 6d^0\ 5f^0$ and $r = 2.67$ (Å), Mn: $4s^2\ 4p^0\ 3d^5\ 4f^0$ and $r = 2.51$ (Å), 2.57 (Å), 2.38 (Å), 2.38(Å), O: $2s^2\ 2p^4\ 3d^0\ 4f^0$ and $r = 1.14$ (Å), Nb: $5s^1\ 5p^0\ 4d^4\ 4f^0$ and $r = 2.89$ (Å), 3.12 (Å), 2.55 (Å), 2.55 (Å), respectively. In order to minimize the Kohn-Sham total energy of the system, the geometric optimization positions of atoms and lattice constants were performed with use of a conjugate gradients method implemented into SIESTA 3.0 code. The tolerance in the maximum atomic forces was set as 0.004 eV/Å and the maximum stress was 0.002 GPa. As a starting point for relaxation was used a unit cell with the perovskite-like structure with free relaxation in each directions and angles of the unit cell.

The structural parameters for BMO at the temperature of 20 K were taken from Ref. [16]. The atom positions in the BMO elementary cell are crystallographically non-equivalent. Therefore, an individual pseudo-potential was ascribed to the each non-equivalent crystallographic position.

In case of BMNO, the stoichiometry condition was obtained when the Mn ions in the non-equivalent positions were replaced by the Nb ions - see Table 1. In such way, two types of the monoclinic structure were obtained. The values of the total energy, the gap energy (E_{gap}), the crystal lattice parameters, the unite volume cell, and differences of spins up and down for the stoichiometric and the defected BMO, BMNO crystals were calculated and presented in Tables 2 and 3. These results were obtained for the two kind of the structure: 1) Nb atoms were placed in 2a and 2b Wyckoff positions, while Mn atoms are in 4c positions, 2) Nb atom in 4c position and Mn atoms in 2a and 2b positions.

The following point defects in the BMO and BMNO crystal structures were considered: oxygen vacancy V_O and bismuth vacancy V_{Bi}, interstitial oxygen O_I, double oxygen vacancies V_O-V_O and interstitial oxygens O_I-O_I placed in the nearest neighbours positions.

3. Results and discussion

The relaxed unit cell of BMO and BMNO in Fig. 1 are presented. The monoclinic symmetries are in accordance with theoretical [9] and experimental [3,10] ones. To achieve the BMNO structure a half of the amount of Mn ions in BMO was replaced by Nb ions. Fig. 1b is described by *case a* in Table 1, Fig. 1c - by *case b* in Table 1.

The calculated total density of states (DOS), obtained for the ideal BMO and BMNO lattices are shown in Fig. 2. The spin up and spin down contributions are shown in Fig. 3. In these figures the energy gap was estimated in the range from 0.2 eV up to 0.5 eV for both crystals (it depends on a value of an integration's step). These values are in a good agreement with the literature data [17]. Results obtained for the second type of the structure (with Nb atom in 4c position and Mn atoms in 2a

Table 1
Starting Wyckoff positions, in agreement to BMO literature data [9,10].

	Wyckoff positions	BMO Fig. 1a	BMNO case a Fig. 1b	BMNO case b Fig. 1c
1	4c	Bi1	Bi1	Bi1
2	4c	Bi2	Bi2	Bi2
3	2a	Mn1	Nb1	Mn1
4	4c	Mn2	Mn2	Nb1
5	2b	Mn3	Nb2	Mn3
6	4c	O1	O1	O1
7	4c	O2	O2	O2
8	4c	O3	O3	O3
9	4c	O4	O4	O4
10	4c	O5	O5	O5
11	4c	O6	O6	O6