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Electronic Structure of the Cubic Perovskites $BiMO_3$ (M = Al, Ga, In, Sc)

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The electronic structure of four cubic perovskites were calculated by using density functional theory. For electronic structure calculations standard generalized gradient approximation and semilocal Tran–Blaha modified Becke–Johnson potential were used. Nonlocal hybrid Heyd–Scuseria–Ernzerhof functional was used to obtain lattice constants and bulk moduli. Standard generalized gradient approximation results are in good agreement with previous calculations but the band gap calculated within TB-mBJ are significantly larger for all compounds. For $BiAlO_3$ this values are: 1.49 eV (GGA) and 2.47 eV (TB-mBJ), $BiGaO_3$: 1.23 eV (GGA) and 2.12 (TB-mBJ), $BiInO_3$: 0.06 eV (GGA) and 0.83 eV (TB-mBJ), $BiScO_3$: 0.70 eV (GGA) and 1.38 eV (TB-mBJ).

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1. Introduction

$BiMO_3$ compounds have attracted a lot of attention due to the many possible applications. The $BiMO_3$ materials with nonmagnetic M ions are considered as possible replacements of Pb-based piezolectric compounds due to similar piezolectric properties but without toxicity of the latter [1, 2]. Bi-based compounds have the stereochemically active $6s^2$ lone pairs which are a source of ferroelectricity (e.g. $BiAlO_3$ [1]). Recently obtained solid solutions of $BiGa_xTM_{1-x}O_3$ with magnetic TM ions (e.g. Cr, Mn, Fe) are considered as possible multiferroics [3]. $BiMO_3$ at room temperature crystallizes in different space groups: $R3c$, orthorombic $Pcca$, $Pna2_1$, and $C2/c$ for M = Al, Ga, In, and Sc, respectively [2].

In this paper we considered only hypothetical cubic structures (Pm-$3m$ space group) of $BiMO_3$ with M = Al, Ga, In, Sc. However in case of $BiScO_3$ the cubic structure coexists with tetragonal phase in $SrTiO_3$–$BiScO_3$ system [4]. The cubic structures of mentioned compounds have been investigated by first-principles method several times [1, 2, 5]. In all these cases the calculations were performed within standard local density or generalized gradient approximations, LDA [6] or GGA [7], respectively. Results obtained by both approximations are in reasonable agreement with experimental data in many cases, however some properties like e.g. band gaps in semiconductors are predicted with huge error (the well-known band gap problem of density functional theory (DFT) which is connected with derivative discontinuity in the exchange-correlation potential see e.g. [8]). To overcome this problem a few more sophisticated and complex methods were developed, for example so-called GW approximation [9] based on many-body perturbation theory or hybrid functionals in which some part of exchange functional from LDA/GGA is replaced by exact exchange calculated within the Hartree–Fock approximation [10]. For solids the most popular hybrid functional is based on the Heyd–Scuseria–Ernzerhof (HSE) formula [11]. The other group of approximations is so-called meta-GGA in which the information from the kinetic energy density is used. The formula proposed by Tran and Blaha which is modified version the Becke–Johnson exchange potential (TB-mBJ) [8] provides a good agreement of band gap values for various semiconducting and insulating systems [12]. The disadvantage of TB-mBJ is that it is not a functional derivative so cannot be used to calculate forces and geometry optimization [13].

In this paper the electronic structure of cubic $BiMO_3$ (M = Al, Ga, In, Sc) within both GGA-PBE and TB-mBJ potential will be presented. We also calculated the lattice constants and bulk moduli for these compounds within both GGA–PBE and hybrid HSE functionals. The latter approach have not been applied in this case yet. According to our knowledge there is no TB-mBJ calculations of band structures for mentioned compounds.

This paper is organized as follows: in next section the short description of the method of calculation is presented, further we present results and discussion and finally short summation is given.

2. Method of calculations

The calculations were done by using the projector augmented wave (PAW) method [14] as implementend in Vienna *ab initio* Simulation Package (VASP) [15]. The Perdew–Becke–Ernzerhof (PBE) generalized gradient approximation [7] was used for exchange-correlation potential. The Brillouin zone integrations were performed by using $12 \times 12 \times 12$ Γ-centered k-point grid. A kinetic energy cutoff of 520 eV and a total energy convergence threshold of 10^{-6} eV were used. The semicore d states were included in valence in Ga and In and as core states

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*corresponding author; e-mail: kaczkowski@ifmpan.poznan.pl in Bi. The lattice constants and bulk moduli were calculated by fitting total energy-volume data obtained within both GGA and HSE potentials to Murnaghan's equation of state [16]. For further studies of electronic structure within semilocal TB-mBJ potential this lattice constants from GGA were taken only.

3. Results

In Table I the lattice constants and bulk moduli were presented. The results obtained by GGA are in good agreement with those obtained in [2]. Values of the lattice constants calculated within hybrid HSE are slightly smaller than those from GGA. For both approximations lattice constants increase and bulk moduli decrease from BiAlO$_3$ to BiInO$_3$. For BiScO$_3$ lattice constant is between values for BiGaO$_3$ and BiInO$_3$. The trend in lattice constants is connected with ionic radii of M atoms which are 67.5, 76, 88.5, and 94 pm for Al, Ga, Sc, and In, respectively [17].

TABLE I

Calculated lattice constants and bulk moduli for BiMO$_3$ by using both GGA and hybrid HSE for exchange-correlation functionals. For comparison data obtained by LAPW method from [2] were taken.

	Lattice constant [Å]			Bulk modulus [GPa]		
	GGA	HSE	GGA [2]	GGA	HSE	GGA [2]
BiAlO$_3$	3.795	3.746	3.802	172.9	196.9	188.5
BiGaO$_3$	3.899	3.847	3.905	153.8	192.5	178.6
BiInO$_3$	4.175	4.120	4.193	134.6	151.2	134.3
BiScO$_3$	4.075	4.033	4.084	137.3	153.1	134.7

TABLE II

Calculated direct and indirect band gaps for BiMO$_3$ by using both GGA and TB-mBJ for exchange-correlation functionals.

	Direct (X)			Indirect (M–X)		
	GGA	TB-mBJ	GGA [2]	GGA	TB-mBJ	GGA [2]
BiAlO$_3$	1.96	2.80	2.07	1.49	2.47	1.57
BiGaO$_3$	1.91	2.69	2.00	1.23	2.12	1.34
BiInO$_3$	1.43	2.09	1.50	0.06	0.83	0.17
BiScO$_3$	0.95	1.86	1.16	0.70	1.38	0.83

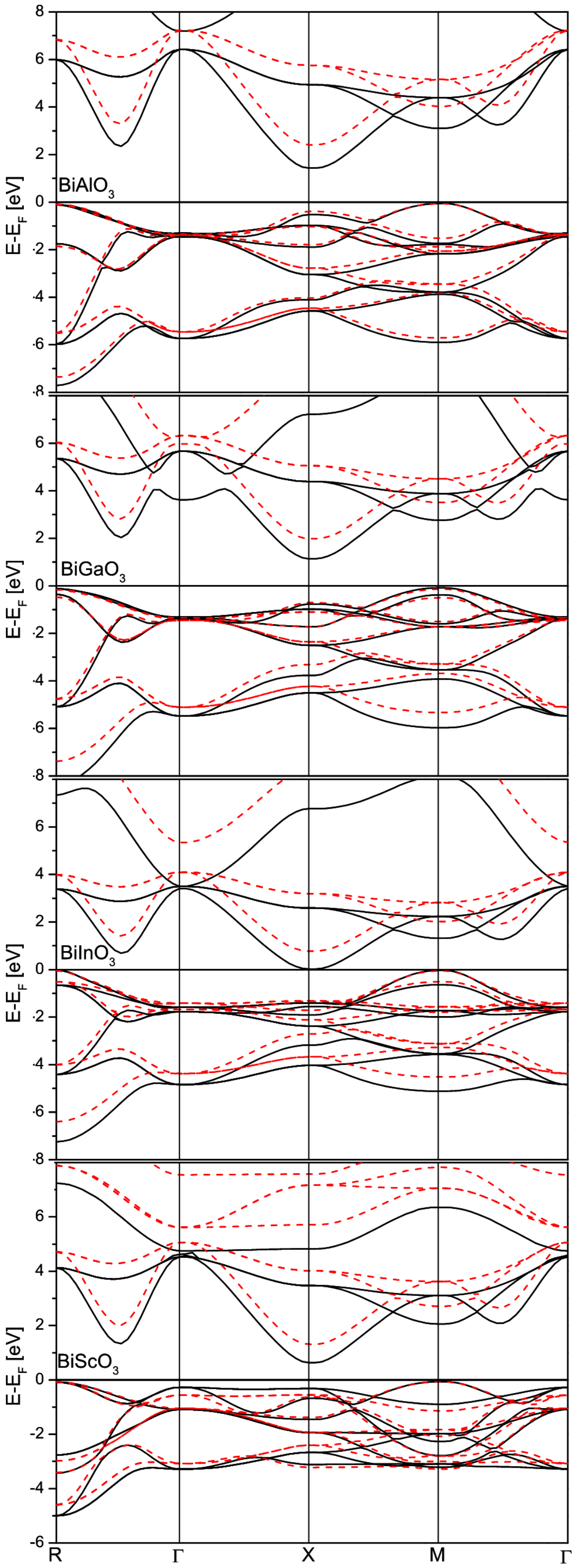

Fig. 1. Band structures of BiAlO$_3$, BiGaO$_3$, BiInO$_3$, and BiScO$_3$ within GGA (black, solid), TB-mBJ (red, dashed).

The band structures along high symmetry directions in the Brillouin zone calculated with GGA–PBE (black-solid) and TB-mBJ (red-dashed) are shown in Fig. 1 and in general are very similar. Band gaps of BiMO$_3$ are given in Table II. In all compounds the band gap remains indirect between M and X and changes from 0.06 (0.83) eV to 1.49 (2.47) eV for BiInO$_3$ to BiAlO$_3$ in GGA (TB-mBJ). The direct gap at X is larger but trend is the same as in case of indirect one. In case of BiAlO$_3$ the indirect band gap obtained within TB-mBJ (2.47 eV) is smaller than calculated by using screened-exchange hybrid functional (3.43 eV) [18]. The valence bandwidth for compounds in GGA are 7.71, 8.34, 7.24, and 5.00 eV for BiAlO$_3$, BiGaO$_3$, BiInO$_3$, and BiScO$_3$, respectively. These values are in good agreement with those in [2]. These values are changed in TB-mBJ and are equal 7.36,

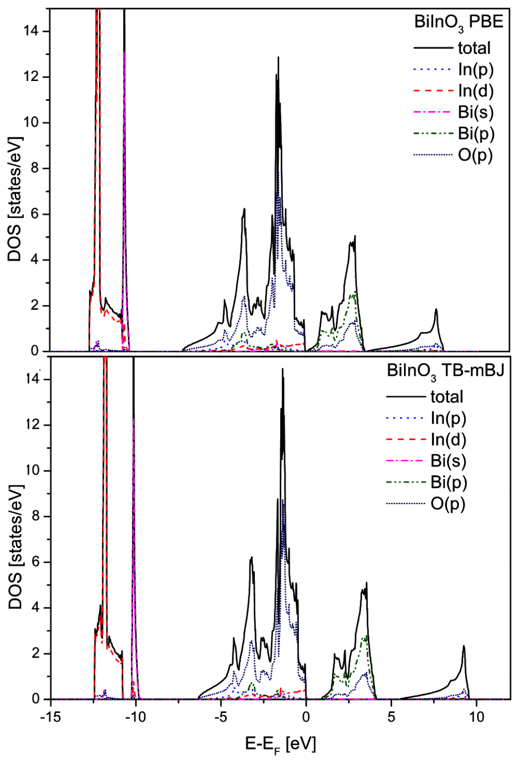

Fig. 2. Density of states for BiInO$_3$ calculated within both GGA-PBE (upper part) and TB-mBJ.

7.38, 6.40, and 4.60 eV for the same order of compounds. The narrowing of valence band and shift of conduction bands to upper values is observed in all compounds. In GGA the obtained values suggested that Ga–O bond is more covalent than in other investigated materials. However in TB-mBJ the value of the bandwidth is similar to the bandwidth of BiAlO$_3$.

As example in Fig. 2 we presented the density of states (DOS) for BiInO$_3$. The valence band maximum consists mainly from O $2p$ states with small contribution from In $4d$ states and main contribution to conduction band comes from Bi $6p$ and O $2p$ orbitals. Lower part of valence band consists of In $4d$ and Bi $2s$ states. These states are shifted to higher values in TB-mBJ.

4. Conclusions

The electronic structure of cubic BiMO$_3$ was presented. The calculations were performed by using GGA and TB-mBJ potential. All compounds are semiconductors with indirect band gap. In all cases the band gaps obtained by the TB-mBJ potential are significantly larger than those calculated within GGA.

Acknowledgments

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