

An *ab initio* study of electronic structure and optical properties of multiferroic perovskites PbVO_3 and BiCoO_3



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ARTICLE INFO

Article history:

Received 17 December 2012

Received in revised form 12 April 2013

Accepted 20 April 2013

Available online 3 June 2013

Keywords:

Density functional theory

FP LAPW

Modified Becke–Johnson potential

Multiferroics

PbVO_3

BiCoO_3

ABSTRACT

Within density functional theory (DFT) with the generalized gradient approximation (GGA), GGA plus on-site Coulomb repulsion method, and improved version of the modified Becke–Johnson exchange potential suggested recently by Tran and Blaha [F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009) 226401] (TB–mBJ), we investigate the electronic structure and optical properties of noncentrosymmetric multiferroic perovskites PbVO_3 and BiCoO_3 . These two compounds, although similar in lattice distortions and population of crystal-field levels, behave quite differently because of the different interplay between the fundamental Kramers degeneracy and the single-ion anisotropy in them. The main characteristic of the calculated TB–mBJ electronic structures is significant rearrangement of the V and Co 3d states near their valence bands tops when compared to the present and earlier GGA and GGA + *U* calculations of these compounds. This fact causes the different optical responses of the title compounds as well, which are analyzed and interpreted in terms of the calculated electronic structures. A comparison of the calculated properties with available experimental data indicates that the TB–mBJ approach provides a better description of the electronic and optical properties of PbVO_3 and BiCoO_3 than the standard GGA and GGA + *U* approaches.

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1. Introduction

Interest in multiferroic (MF) materials has risen enormously in recent years [1]. This especially concerns magneto-electric (ME) multiferroics where magnetic and electric properties are fundamentally coupled [2] and there are prospects of new functionalities important for technical applications.

Recently, simple perovskite-like compounds ABO_3 ($A \in \{\text{Pb}, \text{Bi}\}$; $B \in \{\text{V}, \text{Co}\}$) were synthesized in a bulk and thin film forms under high-temperature and high-pressure conditions, their structural, electrical and magnetic properties were scrutinized and they are regarded as two of the promising candidate MF materials [3–6]. The structural and electronic circumstances in these compounds seem to favour desirable large coupling between a ferroelectricity and a cooperative magnetism [7]. Sizeable ferroelectric polarizations and peculiar magnetic properties [8] are the consequence of large A and B atomic distortions in these materials. Large tetragonal deformations produce layered type structures with semiconducting properties. Off-centre distortions of A ions correlated with significant shifts of B transition metal ions play an important role in producing multiferroism in PbVO_3 and BiCoO_3 .

At the same time both *ab initio* density functional theory and model calculations devoted to structural stability, orbital

hybridization, magnetic ordering and the conditions for the simultaneous appearance of ferroelectricity and ferromagnetism have begun to show up regularly [9–20]. Cited works addressed practically all the important aspects connected with the structural stability and the origin of multiferroism (coexistence and coupling of ferroelectric and (anti)ferromagnetic orderings). These compounds crystallize in the noncentrosymmetric tetragonal crystal structure with the *P4mm* space group. Electronic structure calculations have shown that the most stable state for *both* bulk PbVO_3 and BiCoO_3 is an antiferromagnetic (AF) insulator state with the C-type AF ordering [3,9–11] (for more precise results unattainable by the *ab initio* calculations see below [8]). While for the bulk BiCoO_3 this fact was experimentally confirmed (bulk BiCoO_3 is in the Néel’s AF state below 470 K [5]), experimental results for the bulk PbVO_3 are not so well determined. Namely, magnetic susceptibility measurements with broad maximum around 200 K could be the sign of antiferromagnetism, but no long-range magnetic order was found down to 1.8 K in the neutron-diffraction experiments [3,12]. The results of muon spin rotation measurements have shown the long-range AF ordering below 43 K [6]. In spite of the similar lattice deformations and crystal-field splittings of transition metal levels, these two compounds behave quite differently. First, the calculated easy axes of spin are different: [110] in PbVO_3 and [001] in BiCoO_3 [13]. Then, very nice analysis of such different behaviour and an account of the basic issues for the formation of the spin-spiral magnetic states in PbVO_3 and BiCoO_3 can be found in the recently published

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work of I.V. Solovyev [8]. He showed that the long-periodic spin-spiral state is a probable candidate for the magnetic ground state of PbVO_3 (a system with *odd* number of electrons (1) in the V $3d$ shell) due to the fact that V is a Kramers ion in this compound. For BiCoO_3 (a system with *even* number of electrons (6) in the Co $3d$ shell) the Kramers theorem is no longer applicable so that the spin-spiral state is suppressed by the single-ion anisotropy, which supports the formation of the collinear C-type AF ground state.

It should be mentioned that magnetic ordering in the PbVO_3 thin films seems to be better resolved than in the corresponding bulk compounds. Recent investigations [21] have showed that in the PbVO_3 thin films the G-type AF-structure is realized, mostly due to misfit strain effects that shorten the V–O distances [22]. This effect resolves which one of the almost degenerate C- or G-type AF structures [10] finally prevails in the PbVO_3 thin films. Since the present article deals with the bulk PbVO_3 and employs the same method and computer code as [10], we simulated the C-type AF-structure for the bulk PbVO_3 because this structure was slightly favourable in [10].

At the first sight, it seems that not so much room has been left for new theoretical works about these ME materials. But, the usual approximations used in DFT such as the local density approximation (LDA), generalized gradient approximation (GGA), and $\text{LDA(G-GA)} + U$ have shown different types of insufficiencies when applied to strongly correlated systems. The choice of both the $\text{LDA(G-GA)} + U$ formulation and of the related parameters, usually non-transferable, is a semi-empirical process associated with a loss of predictive power [23]. It is well known that for materials with pronounced electronic correlations a DFT approach produces unsatisfactory band gap and often puts cationic d bands inappropriately when compared to experiments. As a consequence, their interactions with the anionic p valence bands are artificially enlarged and these bands are falsifiably shifted extremely close to the conduction bands. This could be particularly harmful in the systems where both the oxygen hybridization with A and B cationic atoms and their large coordinated off-centering and distortions are crucial for the observed ME behaviour.

The band gap problem was successfully tackled through the DFT calculations with the use of a modified Becke–Johnson (mBJ) [24] exchange potential as proposed by Tran and Blaha (TB) [25]. The new TB–mBJ exchange potential has been used lately by several different groups and they got improved results for electronic properties for a wide range of materials (for a recent estimation of merits and weaknesses of the TB–mBJ approach cf. [26]). The fundamental properties of PbVO_3 and BiCoO_3 , in particular the spin unrestricted electronic band structure, have been extensively investigated by various calculational methods with and without Coulomb correlation corrections included [7–19]. In the present article we will give detailed investigations of the electronic structure and optical properties of PbVO_3 and BiCoO_3 in the (most stable) C-type AF structure and, for PbVO_3 , also in the G-type AF structure, with experimentally observed structural parameters, on the basis of the TB–mBJ exchange potential [25]. The TB–mBJ calculations, when compared with previous results, seem to lead to noticeably better agreement with the known experimental facts.

2. Calculational details

The present calculations were performed in the framework of the full potential linearized augmented plane wave (FP LAPW) method using the WIEN2k program [27]. First of all, we repeated the already obtained results for the electronic structure and linear optical properties of PbVO_3 and BiCoO_3 . The crystal structures of both compounds were taken from the experiment [4], because the optimized atomic positions were found to be very close to the experimental ones [4].

The crystal potentials, electronic wave functions and charge densities were expanded in the basis of (i) linear combinations of radial functions times spherical harmonics inside the non-overlapping muffin-tin (MT) spheres of radii $R_{\text{MT}}(i)$ (i enumerates atoms in the unit cell) centered at each nuclear position, and (ii) plane waves in the interstitial region between the atomic spheres. The MT sphere radii were chosen to be: 2.5, 1.8, and 1.3 Bohrs for Pb, V, and O atoms (PbVO_3), and 2.14, 1.69, and 1.5 Bohrs for Bi, Co, and O atoms (BiCoO_3), respectively.

For the exchange-correlation potential (V_{xc}) we have used

1. Spin-polarized GGA as parametrized by Perdew et al. [28] (we will refer to this calculation as PBE).
2. Spin-polarized GGA (PBE) with the Hubbard type Coulomb correction added, $\text{GGA} + U$ (GGA extension of the so called $\text{LDA} + U$ method suggested by Anisimov et al. [29]; more precisely, we will call it $\text{PBE} + U$) for $U = 3$ eV at the V and Co atoms.
3. $\text{PBE} + U$ for $U = 6$ eV at the V and Co atoms (This method, (i.e. the last two items) partly cured the deficiencies of DFT (namely, GGA alone) in treating Mott–Hubbard or charge transfer insulators).
4. TB–mBJ.

The Kohn–Sham equations were solved self-consistently on a $10 \times 10 \times 10$ (for C-AFM PbVO_3 and BiCoO_3 , and $10 \times 10 \times 6$ for G-AFM PbVO_3) $\mathbf{k}$ -mesh representing 126 (for C-AFM PbVO_3 and BiCoO_3 , and 84 for G-AFM PbVO_3) $\mathbf{k}$ -points in the irreducible wedge of the first Brillouin zone (BZ). The tetrahedron method was used for the BZ integrations. The parameter $\text{RKMAX} := R_{\text{MT}} \cdot K_{\text{MAX}}$, which determines the number of basis functions, is set to be 7.0. R_{MT} is the smallest atomic (MT := Muffin Tin) sphere radius in the unit cell and K_{MAX} is the largest magnitude of the reciprocal lattice vector $\mathbf{K}$ used in the Fourier expansion of the plane waves in the interstitial region (cf. [27]). The Fourier expansion of the charge density is truncated for (norm, or magnitude of $\mathbf{K}$) $\|\mathbf{K}\| = G_{\text{MAX}} = 12 \text{ Bohr}^{-1}$. For the

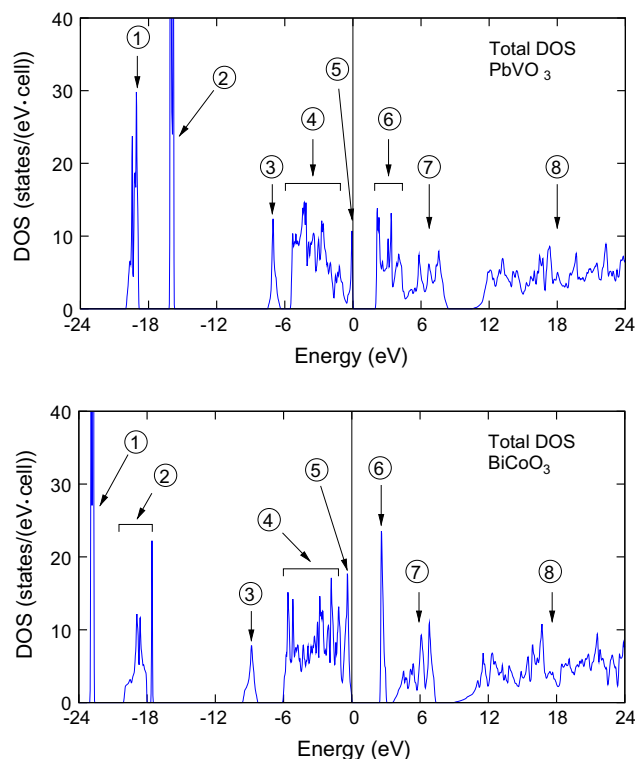


Fig. 1. Total DOS of PbVO_3 (upper panel) and BiCoO_3 (lower panel) calculated with TB–mBJ. Fermi level is at 0 eV.

self-consistency cycle we used two convergence criteria: $\Delta E_{\text{tot}} < 10^{-4}$ Ry and $\Delta q < 10^{-4}e$ (where $e = 1.6 \times 10^{-19}$ C is the elementary charge), both of which should be satisfied for the last few (up to three) consecutive iterations (cf. [27]).

Optical characteristics of PbVO_3 and BiCoO_3 were analyzed in terms of their complex dielectric function (generally speaking, dielectric function ϵ is the function (operator) that transforms electric field $\mathbf{E}$ into dielectric displacement $\mathbf{D}$). Here we confine ourselves to the realm of linear electrodynamics of nondispersive media when dielectric function is a linear operator, or equivalently, second rank tensor. Components of its imaginary part $\text{Im}[\epsilon_{\alpha\beta}]$

($\alpha, \beta \in \{x, y, z\}$) (α and β stand for the components x, y, z of the incident light polarization) are directly proportional to the optical absorption spectrum of the investigated compound. The components $\text{Im}[\epsilon_{\alpha\beta}]$ ($\alpha, \beta \in \{x, y, z\}$) were computed in the framework of the random phase approximation, and neglecting electron polarization effects, using the following formula [30,31]:

$$\text{Im}[\epsilon_{\alpha\beta}(\omega)] = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{i,f} \int_{\text{BZ}} \frac{2d\mathbf{k}}{(2\pi)^3} \langle i, \mathbf{k} | p_\alpha | f, \mathbf{k} \rangle \times \langle f, \mathbf{k} | p_\beta | i, \mathbf{k} \rangle \delta(E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar\omega) \quad (1)$$

for a vertical transition from a filled initial state $|i, \mathbf{k}\rangle$ of energy $E_i(\mathbf{k})$ to an empty final state $|f, \mathbf{k}\rangle$ of energy $E_f(\mathbf{k})$, where ω is the circular frequency of the incident radiation, e the elementary charge, m the electron mass and $\mathbf{p}$ the electron momentum operator.

On the basis of the calculated electronic structure (i.e. knowing the Kohn–Sham orbitals) of PbVO_3 and BiCoO_3 we computed the $\text{Im}[\epsilon_{\alpha\beta}]$ ($\alpha, \beta \in \{x, y, z\}$) up to an incident radiation energy of $\hbar\omega = 40$ eV. The real part of the dielectric tensor is then determined using the Kramers–Kronig relation. Both real and imaginary parts of the dielectric tensor were calculated on a $10 \times 10 \times 10$ (for C-AFM PbVO_3 and BiCoO_3 , and $10 \times 10 \times 6$ for G-AFM PbVO_3) $\mathbf{k}$ -mesh representing 126 (for C-AFM PbVO_3 and BiCoO_3 , and 84 for G-AFM PbVO_3) $\mathbf{k}$ -points in the irreducible wedge of the first BZ, exactly as in the case of the calculation of the electronic structure. All

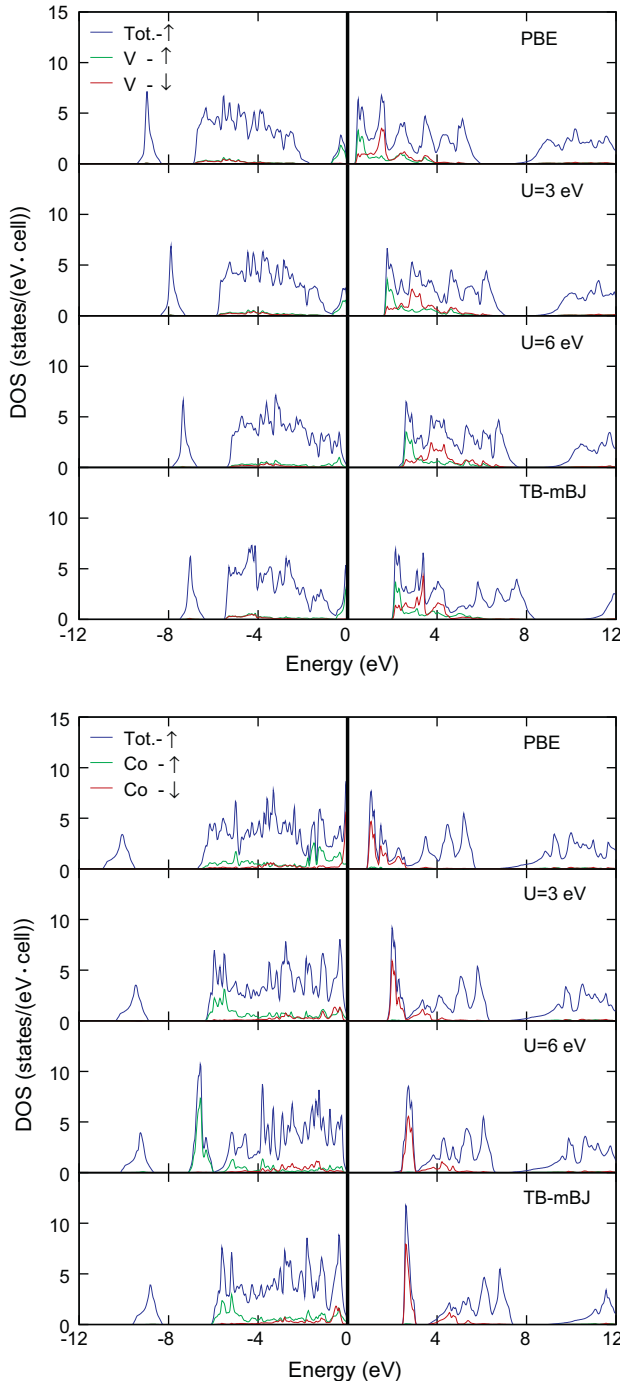


Fig. 2. Total DOS (for spin up states) of PbVO_3 (upper panel) and BiCoO_3 (lower panel) together with the partial DOS's for V and Co in the vicinity of the Fermi level calculated with four different exchange-correlation potentials. Fermi level is at 0 eV.

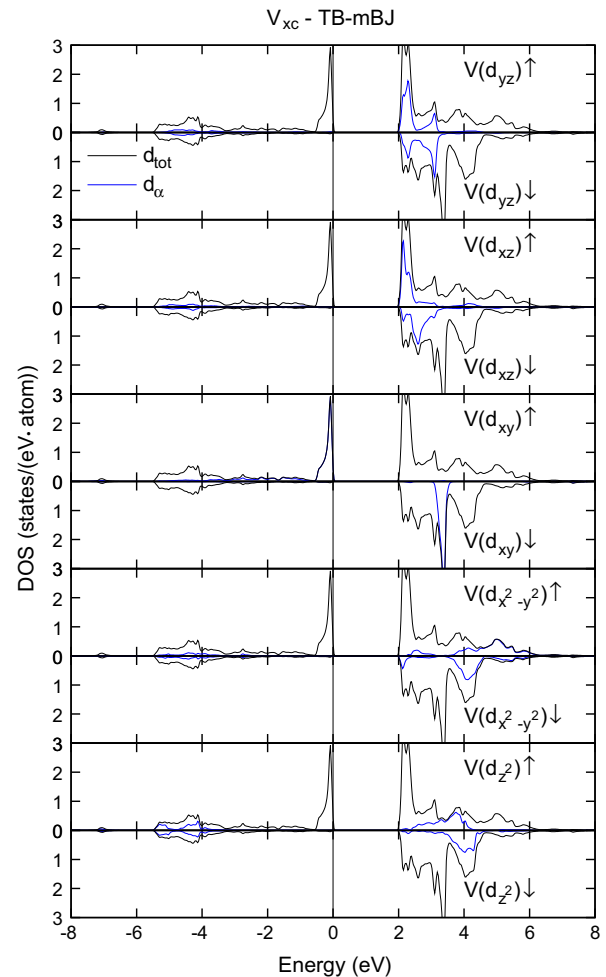


Fig. 3. Partial DOS's, i.e. orbital decomposition of V 3d states of PbVO_3 (blue lines) against the background of the total partial DOS for V 3d states (black lines) in the vicinity of the Fermi level calculated with TB-mBJ ($\alpha \in \{yz, xz, xy, x^2-y^2, z^2\}$). Fermi level is at 0 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the important optical constants of these materials (such as reflectivity, index of refraction, electron energy loss) were then calculated in terms of the real and imaginary part of the dielectric tensor [31]. All graphs were produced with the Lorentzian broadening of 0.06 eV. The scissors operator, which shifts the conduction band bottom, was not applied.

3. Results

3.1. Electronic structure

We determined total and partial densities of states (DOSs) and band structures (along paths consisting of high symmetry direc-

Table 1

Band gap sizes (E_g) and the V and Co magnetic moments, as calculated by the FP LAPW method for PbVO_3 and BiCoO_3 .

	PbVO_3		BiCoO_3	
	E_g (eV)	μ_V (μ_B)	E_g (eV)	μ_{Co} (μ_B)
PBE	0.36	0.79	0.90	2.50
$U = 3$ eV	1.68	0.86	1.70	2.79
$U = 6$ eV	2.31	0.90	1.92	2.98
TB-mBJ	2.01	0.84	2.49	2.96

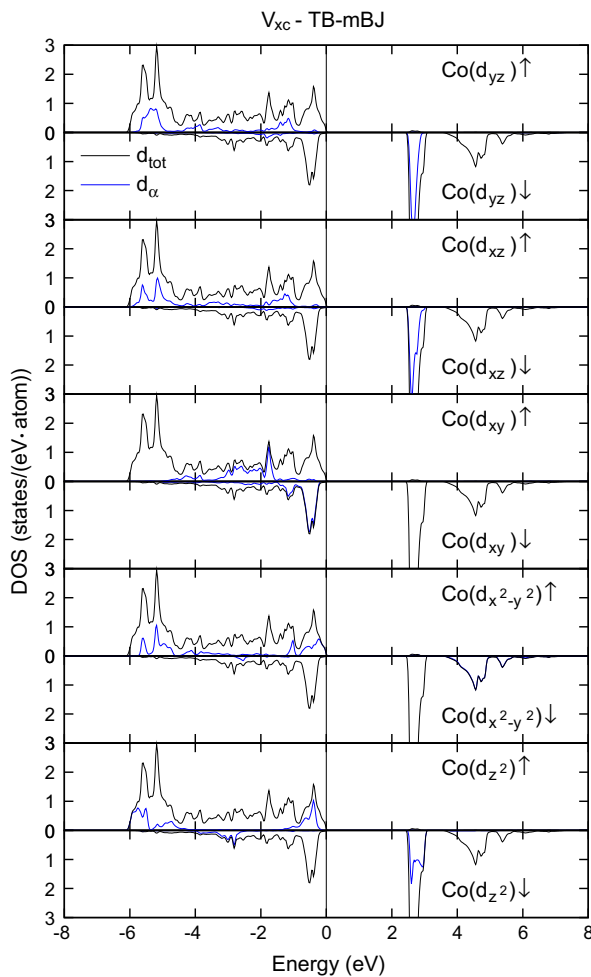


Fig. 4. Partial DOS's, i.e. orbital decomposition of Co 3d states of BiCoO_3 (blue lines) against the background of the total partial DOS for Co 3d states (black lines) in the vicinity of the Fermi level calculated with TB-mBJ ($\alpha \in \{yz, xz, xy, x^2-y^2, z^2\}$). Fermi level is at 0 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tions in the 1st BZ) for both PbVO_3 and BiCoO_3 and for all four types of exchange-correlation potentials listed in Section 2. As mentioned in the introduction, it should be stressed that DFT calculations with GGA-PBE and GGA + U exchange-correlation potentials have already been performed for the two compounds studied in this article. Singh [10] presented his GGA-PBE calculations on the C-type antiferromagnet PbVO_3 , while Uratani et al. [9,13] studied both C-type AFM PbVO_3 and BiCoO_3 , and Cai et al. [11] with LSDA and LSDA + U ($U \in \{3 \text{ eV}, 4 \text{ eV}, 5 \text{ eV}, 6 \text{ eV}\}$). Our PBE and PBE + U results generally agree well with the previously published ones. To maintain a balance between the amount of figures and text we will present results mostly just for the TB-mBJ exchange-correlation potential.

Fig. 1 shows total densities of electronic states of PbVO_3 and BiCoO_3 in a wide energy interval $[-24 \text{ eV}, 24 \text{ eV}]$ symmetric around the Fermi level, calculated with the TB-mBJ exchange-correlation potential.

For PbVO_3 , the first group of states marked with number 1 (GoS 1) consists mainly of O($2s^2$) states (6 electrons, since there are 3 O atoms in the formula unit). GoS 2 consists mainly of Pb($5d^{10}$) states (10 electrons). GoS 3 consists mainly of Pb($6s^2$) states (2 electrons). GoS 4 consists mainly of O($2p^6$) states (18 electrons). GoS 5 (which is at the top of the valence band) consists mainly of a single V($3d$) state (1 electron) while GoS 6 (which is at the bottom of the conduction band) consists of the rest of the V($3d$) states (9 empty states). GoS 7 consists mainly of Pb($6p^6$) states (6 empty states). GoS 8 (approximately above 11 eV) come mainly from the states from the interstitial region (24 empty states).

For BiCoO_3 , (taking into account that now Bi takes the role of Pb, while Co takes the role of V) there are two main differences compared to PbVO_3 . The first is that GoS 1 now consists mainly of

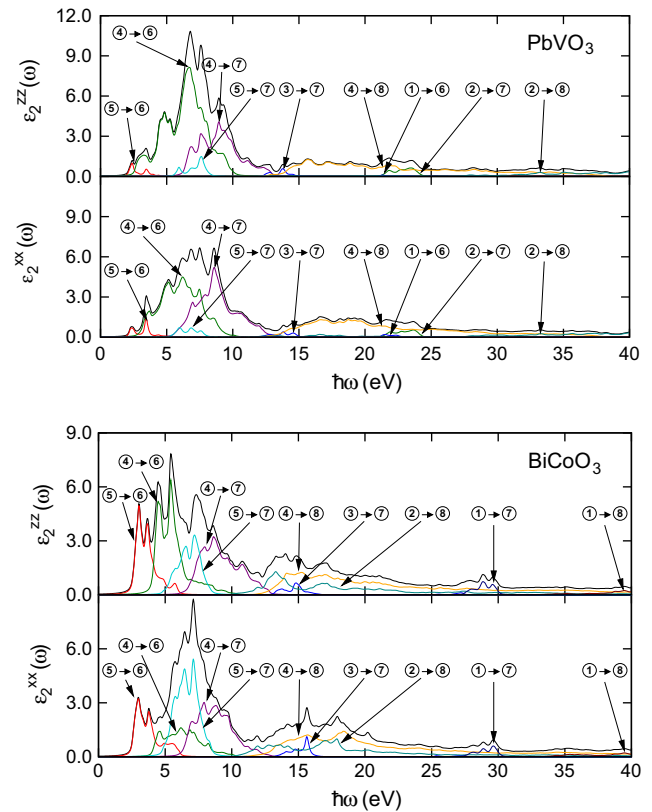


Fig. 5. Imaginary parts (full black lines) of the dielectric tensors for PbVO_3 (upper panel) and BiCoO_3 (lower panel) calculated along two different crystal directions with the TB-mBJ exchange potential. They are decomposed and interpreted in terms of the electronic structure presented in Fig. 1.

Bi($5d^{10}$) states (10 electrons), while GoS 2 consists mainly of O($2s^2$) states (6 electrons) (i.e. they have been interchanged). GoS 3 consists mainly of Bi($6s^2$) states (2 electrons). GoS 4 consists mainly of O($2p^6$) states (18 electrons). The second main difference is in the number of filled Co($3d$) states – GoS 5 (which is at the top of the valence band) consists mainly of Co($3d$) states (6 electrons) while GoS 6 (which is at the bottom of the conduction band) consists of the rest of the Co($3d$) states (4 empty states). GoS 7 consists mainly of Bi($6p^6$) states (6 empty states). GoS 8 (approximately above 9 eV) come mainly from the states from the interstitial region (86 empty states).

Comparison of the electronic structure for different exchange-correlation potentials is presented in Fig. 2. While both PBE + U and TB-mBJ widen the gap between the highest valence and lowest conduction band, TB-mBJ pushes the states upward in energy, in particular, it pushes the states that are below the Fermi level towards the Fermi level.

Values for the band energy gap and magnetic moments obtained with different exchange-correlation potentials are given in Table 1. For BiCoO₃, μ_{Co} calculated using PBE + U and TB-mBJ agrees well with the experimentally measured value $3.24 \mu_B$ [14].

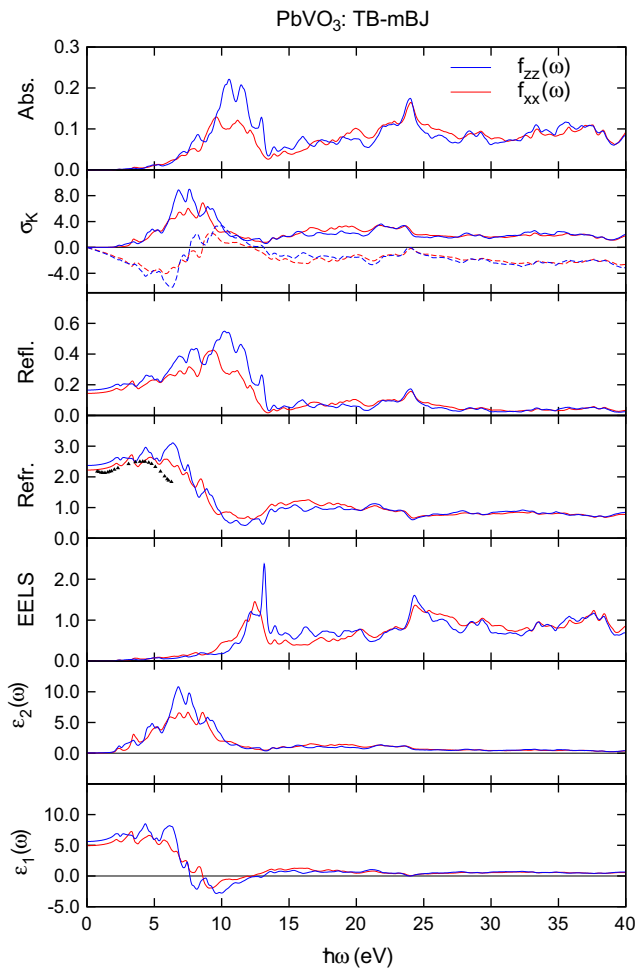


Fig. 6. Optical coefficients of PbVO₃ calculated with TB-mBJ. xx components are labeled red, zz components are labeled blue. From bottom to top: $\epsilon_1(=Re[\epsilon])$, $\epsilon_2(=Im[\epsilon])$, electron energy loss, refractive index, reflectivity, optical conductivity ($Re[(\sigma_K)_{xx}]$ is red full line, $Im[(\sigma_K)_{xx}]$ is red dashed line, $Re[(\sigma_K)_{zz}]$ is blue full line and $Im[(\sigma_K)_{zz}]$ is blue dashed line), absorption coefficient. For the index of refraction of PbVO₃, 23 experimental points taken from the graph in Fig. 1 from [32] have been superimposed (as black triangles pointing up). This is shown again in Fig. 8 compared with the other three exchange-correlation potentials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Orbital decompositions of V $3d$ states of PbVO₃ and of Co $3d$ states of BiCoO₃ in the vicinity of the Fermi level calculated with TB-mBJ are shown next in Fig. 3 and Fig. 4. It can be seen that TB-mBJ as compared to PBE + U correctly puts the minority spin Co $3d$ xy orbital (the only occupied minority spin Co $3d$ orbital) close to the top of the valence band (cf. Fig. 4 in [13]).

3.2. Optical properties

As described above, we have calculated the complex dielectric tensors of PbVO₃ and BiCoO₃ as well as several other optical coefficients in the energy region of up to 40 eV (here energy represents the energy of the incident light which corresponds to the difference between the two energy levels of the title compounds). For the given tetragonal crystal structure of PbVO₃ and BiCoO₃, xx and yy components of the coefficients coincide, while zz is different. Hence, in the figures that follow we present only xx and zz components. Since the theoretically calculated optical properties for C-type and G-type AF structure of PbVO₃ are very similar, in what follows for PbVO₃ we show results only for the C-type AF structure without explicitly mentioning so. Only in the last two figures (Figs. 8 and 9) when we make comparison with the experiment we also show results for the G-type AFM PbVO₃.

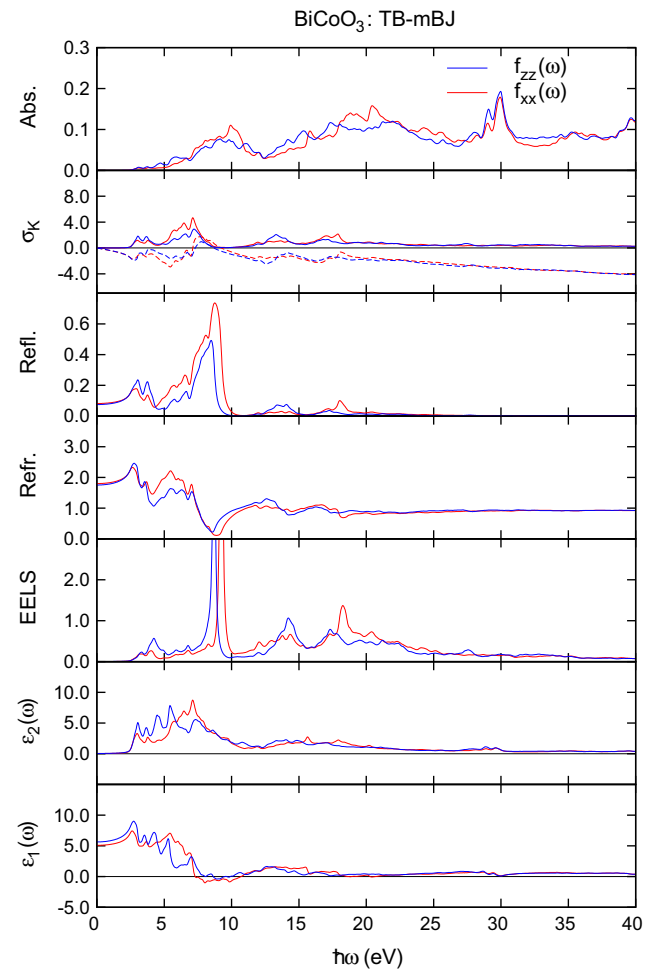


Fig. 7. Optical coefficients of BiCoO₃ calculated with TB-mBJ. xx components are labeled red, zz components are labeled blue. From bottom to top: $\epsilon_1(=Re[\epsilon])$, $\epsilon_2(=Im[\epsilon])$, electron energy loss, refractive index, reflectivity, optical conductivity ($Re[(\sigma_K)_{xx}]$ is red full line, $Im[(\sigma_K)_{xx}]$ is red dashed line, $Re[(\sigma_K)_{zz}]$ is blue full line and $Im[(\sigma_K)_{zz}]$ is blue dashed line), absorption coefficient. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

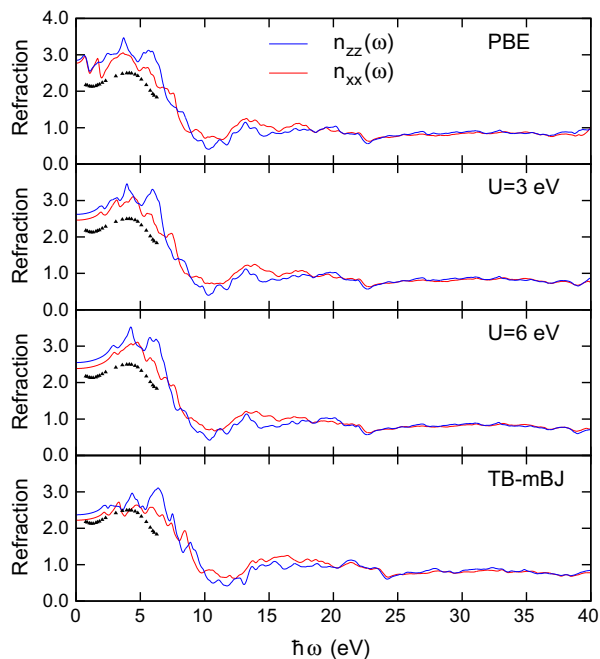


Fig. 8. Index of refraction of **C-AFM** PbVO_3 calculated with four different exchange-correlation potentials and compared with the experimental results: in each of the four panels of Fig. 8, 23 experimental points taken from the graph in Fig. 1 from [32] (representing measured index of refraction) have been superimposed (as black triangles pointing up) on the theoretically calculated index of refraction. xx component is labeled red, zz component is labeled blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

First we show imaginary parts of the dielectric tensors for PbVO_3 and BiCoO_3 calculated along two different crystal directions with the TB-mBJ exchange potential (Fig. 5). They are directly proportional to the corresponding optical absorption of light polarized along these directions. They are decomposed and interpreted in terms of the electronic structure presented in Fig. 1. Namely, since in the chosen energy interval $[-24 \text{ eV}, 24 \text{ eV}]$ there are 5 groups of states below the Fermi level and 3 groups of states above the Fermi level, there are 15 possible transitions ($1 \rightarrow 6, 1 \rightarrow 7, \dots, 5 \rightarrow 8$). Out of these 15 transitions we have chosen to show 9 most significant (which by themselves already almost completely add up to the full curves (black lines in Fig. 5) that represent the total imaginary parts of the dielectric tensors).

Fig. 5 demonstrates that most intense, lowest energy part of the optical absorption spectrum in both compounds is almost completely determined by the electronic transitions within the BO_5 rectangular pyramid ($B \in \{\text{V}, \text{Co}\}$). The very first peak in the PbVO_3 spectrum is dominated by the $V-d$ to $V-d$ transitions, while the consequent peaks originate from the transitions from populated neighbouring $O-p$ states to the empty $V-d$ states (see Figs. 1 and 5). Very similar conclusions can be drawn for the BiCoO_3 optical absorption spectrum. The lowest energy peak is generated by electronic transitions from empty to populated Co d -states, while the consequent peaks are dominated by electron transfer from the $O-p$ to the Co- d states. Since both crystal structures are noncentrosymmetric, $d-d$ transitions are not dipole-forbidden. Figs. 6 and 7 present various optical constants of PbVO_3 and BiCoO_3 , calculated as functions of incident radiation energy up to 40 eV. As almost all of them have not been studied experimentally yet, these figures should be understood as theoretical predictions.

Finally, for PbVO_3 we are able to make comparison with the experiment [32] where refraction index (n) and extinction coefficient (k) were measured in PbVO_3 thin films over a spectral range

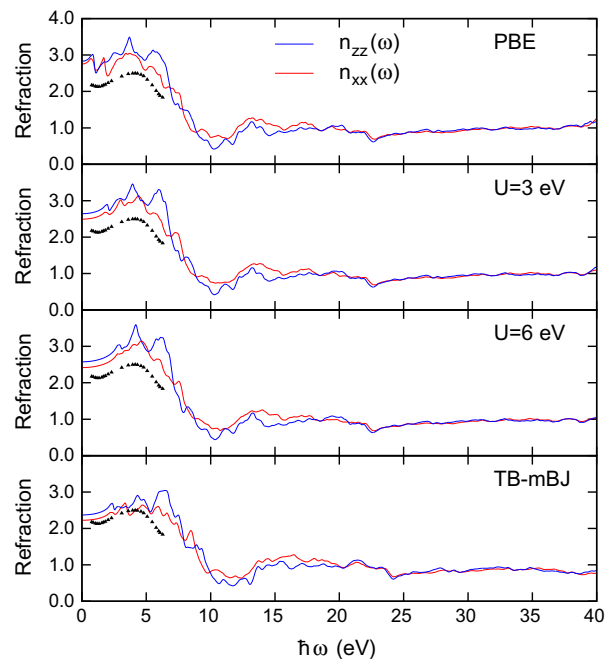


Fig. 9. Index of refraction of **G-AFM** PbVO_3 calculated with four different exchange-correlation potentials and compared with the experimental results: in each of the four panels of Fig. 8, 23 experimental points taken from the graph in Fig. 1 from [32] (representing measured index of refraction) have been superimposed (as black triangles pointing up) on the theoretically calculated index of refraction. xx component is labeled red, zz component is labeled blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

from 200 nm to 1670 nm (0.775 eV to 6.199 eV). The thin film properties can be different from the bulk properties (which were calculated in this article) due to finite-size effects present in the film. The magnitude of differences depends on the thickness of the film (which can be as thick as several micrometres) and on the physical property which is studied. In the Ref. [32] the authors do not report the thickness of their thin film, but use the parameters of the bulk thickness to extract refraction data from the experimentally recorded ellipsometric spectrum. Furthermore, the optical characteristics of the film depend primarily on the bonding between the atoms, which should not be very much affected by its finite thickness. As a consequence, the bulk refraction spectrum is expected to be comparable to the one recorded from the thin film. In each of the four panels of Figs. 8 and 9, 23 experimental points from the graph in Fig. 1 from [32] (representing measured index of refraction) have been superimposed (as black triangles pointing up) on the theoretically calculated index of refraction. It is clearly seen that, when compared with the other three exchange-correlation potentials, TB-mBJ gives better agreement with the experiment.

4. Conclusions

We have calculated electronic and optical properties of magnetoelectric multiferroic perovskites PbVO_3 and BiCoO_3 using DFT with four different exchange-correlation potentials. Among them, for the first time for these compounds, TB-mBJ has been used. It can be seen (from our results) that TB-mBJ although computationally relatively cheap gives improved results when compared to PBE and PBE + U . In particular, spectral weight distribution and the position of occupied transition metal d -states are better than for PBE and PBE + U . Appropriate band gap values are obtained, and for PbVO_3 , index of refraction, calculated with TB-mBJ is in better

agreement with the experiment than refractive indices calculated with the other three exchange-correlation potentials.

Acknowledgments

Financial support for this study was granted by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 171033). M.V. Lalić gratefully acknowledges CNPq and CAPES (Brazilian funding agencies) for financial help.

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