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Ab initio study on magnetoelectric and electronic properties in Pb_2TiVO_6

Feng Hong-Jian(冯宏剑)† and Liu Fa-Min(刘发民)‡

School of Science, Beijing University of Aeronautics and Astronautics, Beijing 100191, *China*

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First principles calculations within the projected augmented-wave (PAW) method, using the local spin density approximation plus U (LSDA+U) scheme, show that the tetragonal Pb_2TiVO_6 is a potential multiferroic material with antiferromagnetic (AFM) spin configuration. It has a magnetic moment of 1 μ_B in a one unit cell originating from the non-bonding orbital d_{xy} in a majority spin channel and a band gap of 1.45 eV with proper U. The large BEC (Born effective charge) of Pb and Ti shows that the stereochemical activity of Pb and Ti may provide the possibility of switchable paths for the ferroelectricity in this hypothetical material. The insulating property and the lower resistivity in the recent prepared $PbVO_3$ can be significantly improved by adopting the Ti.

Keywords: multiferroics, density functional theory, density of states, Pb_2TiVO_6
PACC: 7115, 7510, 7780

1. Introduction

Multiferroic magnetoelectrics have attracted much attention in terms of their magnetoelectric effect in which the electric polarization can be reversed by the inversion of magnetic field, and *vice versa*.[1−6] Their potential applications in information storage and emerging spintronics make them a hot spot in multifunctional materials. Recently, Shpanchenko and co-workers have prepared $P4mm$ $PbVO_3$ with application of a high-pressure high-temperature technique.[7] $PbVO_3$ should be a potential magnetoelectric material in that it is composed of a magnetic V^{4+} ion with an excess electron in d orbitals. ABO_3 perovskite ferroelectrics have been studied intensively for decades due to their simple structure within density functional theory (DFT).[8,9] There are two kinds of ferroelectric mechanisms in classic ferroelectrics such as $BaTiO_3$, $PbTiO_3$, and $BiFeO_3$: one is the off-centre displacement of transition metal ions in a B site caused by M (transition metal ions) 3d-O 2p hybridization, the other is the stereochemical activity of a lone-pair of $(ns)^2$ electrons in A site. The off-centre distortion of small transition metal ions always requires that the d orbitals are unoccupied, thus the "d^0-ness" criteria definitely precludes the magnetism in these ferroelectrics.[10] However, in multiferroic such as $BiFeO_3$, the polarization is mainly caused by the activity of the lone-pair of $(6s)^2$ electrons in the A site while leaving excess electrons in d orbitals in the B site, and the ferroelectricity and the weak ferromagnetism can coexist in this case. The same ferroelectric mechanism occurs in $PbVO_3$, this offers the possibility of combining a B-site magnetic ions with insulating behavior and off-centring displacements of both A- and B-sites. We suggest it is a potential magnetoelectric material in which the coexistence of ferroelectricity and magnetism can occur, provided that the ferroelectric behavior can be observed by substitution in the B site.

Based on the linearized muffin-tin orbital method with the atomic spheres approximation (LMTO-ASA), they also reported the local spin density approximation (LSDA) electronic structure calculations. Due to the basis set errors of this method in highly non-cubic site symmetries as in $PbVO_3$, they predicted an insulating characteristic strongly depending on the electron correlation potential and a spin moment of 0.74 μ_B. It was improved by Singh using the general potential linearized augmented plane wave (LAPW) method having a much better basis set than the LMTO-ASA method,[11] and a spin moment of 1 μ_B was reported for the ferromagetic structure due to the Hund's coupling and the exchange splitting. Unfortunately, the electric polarization still can-

†E-mail: fenghongjian@gmail.com
‡E-mail: fmliu@buaa.edu.cn

not be observed. The ferroelectric property might be achieved by chemical modification proposed in Ref.[11]. Previously we have succeeded in predicting a multiferroic Bi_2FeTiO_6 by partly substituting Fe by Ti in $R3c$ $BiFeO_3$ along the [1 1 1] crystal direction and systematically investigated the magnetoelectric properties in these series of materials.[12−15] Motivated by our previous work, here we report a local spin density approximation (LSDA) and LSDA+U calculations using a projected augmented-wave (PAW) method within DFT on tetragonal Pb_2TiVO_6 with partly substituting V by Ti in $PbVO_3$. We mainly considered the substitution in the ab plane where a two-dimensional $PbVO_3$ structure was cut through by the Ti layer inserted which may decrease electron hopping in the ab plane and improve the insulating property consequently. Moreover, the Ti is more switchable than V, and is able to produce a more switchable polarization out of plane which is the key issue needed to be solved in $PbVO_3$. The magnetic ordering, ferroelectric, and electronic property for the new system have been analyzed here. The remainder of this article is organized as follows: In Section 2, we present the computational details of our calculations. In Section 3, we report the calculated results and discussions. In Section 4, the conclusions based on our calculations are given.

2. Computational details

Calculations in this work have been done using the ABINIT package.[16,17] LDA of the exchange correlation functional was approximated using Perdew–Zunger parametrization of Cerperly–Alder data. LDA or generalized gradient approximation (GGA) within DFT always underestimates the band gap in transition-metal oxides, and a Hubbard-like term U is introduced in the total energy to give a better description of the electronic correlations in the transition-metal ions. LSDA+U within the projected augmented-wave (PAW) method implemented in the package were used to treat the correlated orbitals in the transition metals.[18−23] The parameters for the PAW datasets are summarized in Table 1. Two partial waves per l quantum number were used. $10 \times 10 \times 10$ Monkhorst–Pack sampling of the Brillouin zone is used for all calculations. A plane-wave basis set with a kinetic energy cut-off of 30 Hartree was employed. We took the atomic parameters from Ref.[7] to build the non-spin (NS) structure. Collinear spin configurations have been used to construct the different magnetic configurations, such as ferromagnetic (FM), and antiferromagnetic (AFM) structure along z direction where we doubled the unit cell. In the modern theory of polarization, the total polarization $\boldsymbol{P}$ for a given crystalline geometry can be calculated as the sum of ionic and electronic contributions.[24−26]

Table 1. Parameters of the PAW datasets used in the present work. r_c^l are the cutoff radii for the partial waves.

	valence orbitals	r_c^l/a.u.
O	$2s2p$	1.1
Ti	$3p4s4p3d$	2.3
V	$3p4s4p3d$	2.3
Pb	$5d6s6p$	2.5

3. Results and discussion

The lattice parameter is optimized with the volume varying from from 98.2797 Å^3 to 198.8073 Å^3 (1 Å=0.1 nm). The relation between the total energy and unit cell volume is shown in Fig.1. The data are fitted to the Murnaghan EOS, which are also presented in the figure. The values of a and b are increased as compared with the one of 3.8001 Å in $PbVO_3$[7] while the c/a ratio is decreased. This is caused by the substitution of Ti in plane and the use of the LDA exchange correlation functional. The smaller c/a ratio makes the ferroelectric reorientation possible in the new system. The internal coordinations are fully relaxed with the optimized lattice parameter, and the results are shown in Table 2. All the atoms, including the cations and anions, are all moving slightly in the z direction, while leaving the x, y positions even unchanged. We suggest that the strong hybridization between Ti and V $3d$ and O $2p$ along z induces the deviation in this direction.

Table 2. Relaxed lattice parameters and Wyckoff positions.

a/Å	b/Å	c/Å		Wyckoff positions
7.6595	3.8111	3.8716	Pb(1a)	(0.25,0.5,0.4572)/(0.75,0.5,0.4572)
			Ti/V(1b)	(0.5,0,–0.0573)/(0,0,–0.0588)
			O1(1b)	(0,0,0.4332)/(0.5,0,0.4326)
			O2(2c)	(0.25,0,0.9320)/(0.75,0.5,0.9320)/(0,0.5,9319)/(0.5,0.5,0.9203)

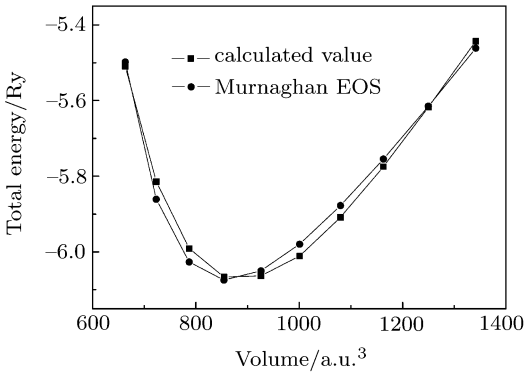


Fig.1. Unit cell volume vs. energy.

For comparison, we took $PbVO_3$ as a reference structure. The AFM spin configuration was arranged with the unit cell being doubled along the z direction. The total energy in the unit cell corresponding to AFM, FM, and NS magnetic configurations for $PbVO_3$ and Pb_2TiVO_6 were reported in Table 3. Calculated total energy shows that the FM supercells for Pb_2TiVO_6 have a relatively higher energy of 5 meV and 116 meV corresponding to the NS and AFM configuration, respectively. Apparently, the AFM configuration is energetically favorable, and the same trend is true for $PbVO_3$.

Table 3. Total energy per formula unit for $PbVO_3$ and Pb_2TiVO_6 with a different spin configuration.

E/eV	NS	FM	AFM
$PbVO_3$	–40.7204	–40.7985	–40.7996
Pb_2TiVO_6	–82.6019	–82.5962	–82.7122

Considering the Coulomb on-site interaction, the DFT+U treats the localized electrons in the transition metal ions properly and improves the calculated values close to the experimental results. However, LSDA+U is a crude method to apply, and a reasonable value should be chosen so that the results calculated are close to the experiments with the value of U varying in a certain range. Here, we had U varied from 0 eV to 7 eV. The magnetic moment per formula unit for $PbVO_3$ and Pb_2TiVO_6 in FM state as a function of U is illustrated in Fig.2. In Pb_2TiVO_6, the magnetic moment is increasing to 1 μ_B which is close to the experimental value[7] as U is approaching 4 eV. This indicates that the Hubbard interaction takes great effect on the spin configuration. There is a small fluctuation of magnetization around 1 μ_B in $PbVO_3$ with U in the range from 0 eV to 7 eV. We suggest that the introduction of Ti, then the interaction between Ti and V in *ab* plane, may shift some bands in V near the Fermi level, and this Ti-V interaction strongly depends on the Hubbard parameter.

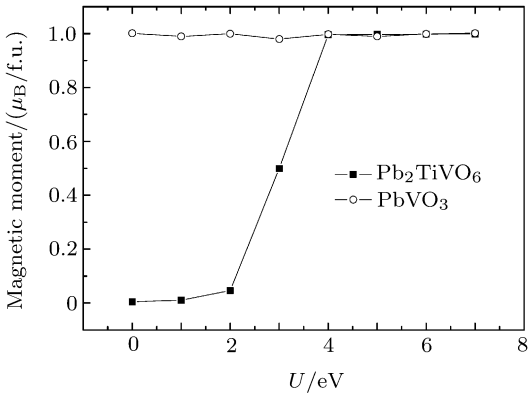


Fig.2. Magnetic moment for $PbVO_3$ and Pb_2TiVO_6 as a function of U.

The relation between the band gap and U is shown in Fig.3. The insulating property in Pb_2TiVO_6 is improved significantly in comparison with $PbVO_3$. It can partly reflect the fact that the Ti layer inserted would destroy the two-dimensional structure in the *ab* plane and sharply impede the conductive property of electrons jumping in the plane. A band gap is introduced in Pb_2TiVO_6 with AFM spin configuration even without applying U, and the band gap increases monotonically with U increasing. Moreover, the AFM spin configuration has a relative large band gap compared with the FM one, indicating that the ground state AFM state exhibits a better insulating property than the NS and FM magnetic arrangement. As U is close to 4 eV, a band gap of 1.2 eV can be obtained, and the curve becomes flat when U is passing through 4 eV. Therefore, U is chosen to be 4 eV for V in the following sections.[7]

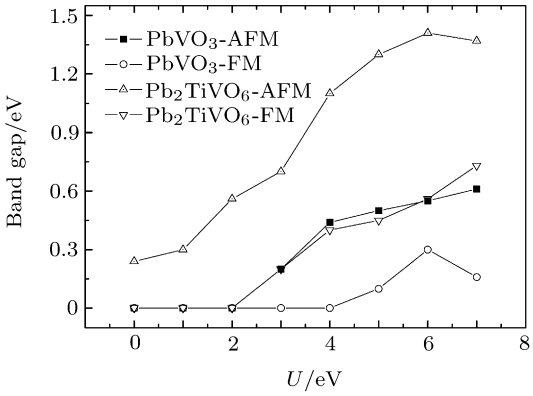


Fig.3. Band gap for $PbVO_3$ and Pb_2TiVO_6 as a function of U.

In order to analyze the electronic property for $PbVO_3$ and Pb_2TiVO_6 with application of U, the total density of states (DOS) and orbital-resolved DOS (ODOS) of V for Pb_2TiVO_6 and $PbVO_3$ in AFM spin configuration with and without application of U are shown in Figs.4(a)–4(h), respectively. From the total DOS it is clear that the manifold states near the Fermi level are mainly attributed to the transition-metal ions. Under the oxygen octahedra crystal field, the $3d$ states of the transition-metal ions are split into two groups: lower lying t_{2g} states, and higher lying e_g states. They are split further with off-centre displacement of the V and Ti ions. Generally, the V d orbitals are anti-bonding, and the e_g states are further split into d_{z^2}, and $d_{x^2-y^2}$ orbitals while t_{2g} states are split into a lower lying d_{xy} non-bonding band and a higher lying two fold degenerate d_{yz}, d_{xz} bands. From the DOS and orbital-resolved DOS (ODOS) of V in $PbVO_3$ (Figs.4(e) and 4(f)), the crystal field splitting is not sufficient to open a gap between the minority spin d_{xy} band and the higher lying d bands, and a gap of 0.4 eV is observed with applying U of 4 eV.

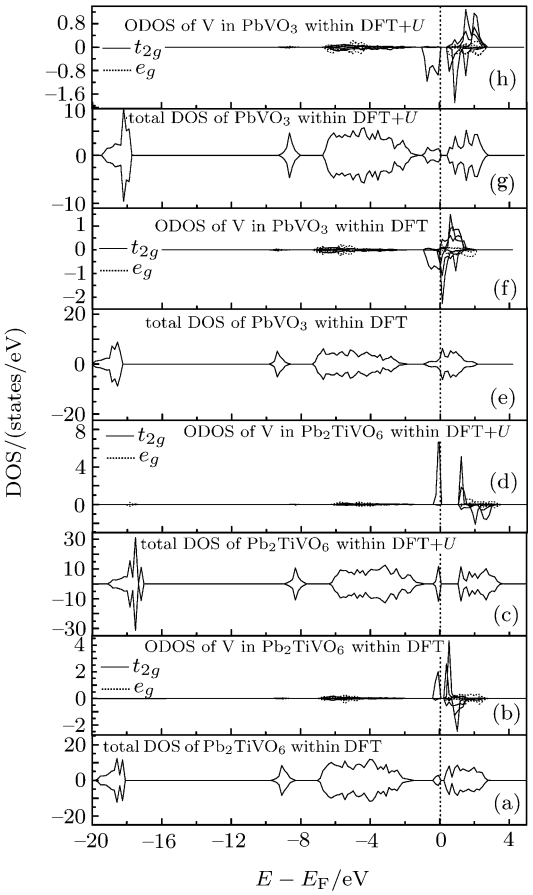


Fig.4. Total DOS and ODOS of V for Pb_2TiVO_6 and $PbVO_3$ in AFM spin configuration within DFT and DFT+U. The Fermi level is set to zero.

This is mainly due to the bandwidth of d_{xy} band in $PbVO_3$. However, in Pb_2TiVO_6 (Figs.4(a) and 4(b)) with Ti inserting in-plane, the main hopping is disrupted in the ab plane, leading to the narrow d_{xy} band in majority spin channel. On the other hand, the AFM spin configuration also increases the exchange splitting energy by disrupting the nearest neighbor hopping in-plane, resulting in a narrow majority spin d_{xy} band. Therefore, the AFM Pb_2TiVO_6 exhibits a good insulating property compared with $PbVO_3$, the band gap is increased from 0.25 eV to 1.1 eV (Figs.4(c) and 4(d)) by pushing d_{z^2}, $d_{x^2-y^2}$, d_{yz}, and d_{xz} bands away from the Fermi level when the Hubbard parameter was considered, while a gap of 0.45 eV (Figs.4(g) and 4(h)) can be obtained in $PbVO_3$ by the shift of t_{2g} and e_g with U being applied. From the ODOS of V in Pb_2TiVO_6 (Fig.4(d)), it exhibits a classic oxidation state of V^{4+}, and only non-bonding orbital d_{xy} is occupied with majority spin electrons while all the other orbitals are empty, leading to a net weak spin moment caused by Hund's coupling.

The spontaneous polarization was evaluated using the Berry phase method based on the modern theory of polarization.[24−26] The change of electric polarization, $\boldsymbol{P}$, is calculated from the Berry phase method by considering a specific structural pathway parameterized by the change in atomic displacement connecting a centrosymmetric reference structure and the displaced $P4mm$ structure. In periodic gauge,

$$\Delta P_\alpha = -\frac{\mathrm{i}fQ_e}{8\pi^3}\sum_{n=1}^{M}\int_{\mathrm{BZ}}\mathrm{d}q\Big\{[\langle u_{q,n}^{(\lambda)}|\partial/\partial q_\alpha|u_{q,n}^{(\lambda)}\rangle]|_0^1 - \int_0^1 \mathrm{d}\lambda\frac{\partial}{q_\alpha}\langle u_{q,n}^{(\lambda)}|\partial/\partial\lambda|u_{q,n}^{(\lambda)}\Big\}, \quad (1)$$

in terms of cell-periodic function $u_{q,n}^{(\lambda)}$. The second term has no contribution. In the actual calculation, we choose a direction parallel to a certain reciprocal lattice vector, the discrete form is

$$P_{\parallel}^{(\lambda)} = -\left(\frac{fQ_e}{8\pi^3}\right)\int \mathrm{d}q_\perp\phi^{(\lambda)}(q_\perp), \quad (2)$$

here

$$\phi_j^{(\lambda)}(q_\perp) = \mathrm{Im}\Big\{\ln\prod_{j=0}^{J-1}\det(\langle u_{q_{j,m}}^{(\lambda)}|u_{q_{j+1,m}}^{(\lambda)}\rangle)\Big\}. \quad (3)$$

We used a set of strings of eight k points parallel to the third reciprocal lattice vector to calculate the electric polarization, and a spontaneous polarization of 42.67 μC/cm^2 is obtained from the method above. The value of polarization is smaller than that in $PbTiO_3$, and this may partly reflect the fact that

there are bond competitions among Pb-O, V-O, and Ti-O so that the activity of the lone-pair of $(6s)^2$ of Pb^{2+} is decreased.

Born effective charge (BEC) ($Z^\star$) governs the amplitude of the long-range Coulomb interaction between nuclei and the splitting between longitudinal optic (LO) and transverse optic (TO) phonon modes. The dynamical BEC tensor ($Z^\star$) of a given ion is the total macroscopic current adiabatically transported by the ion moving with unit velocity, while all the other ions and the macroscopic field remain fixed. It can be calculated within density functional perturbation theory (DFPT).[27] The BEC tensor ($Z^\star$) for Pb, Ti, V, and O are shown in Table 4. The anomaly of BEC ($Z^\star$) for Ti shows that it contributes significantly to the ferroelectricity in the new system, while the BEC for Pb and V is also greater than the nominal charges indicating the hybridization with O and the contribution to the electric polarization. Moreover, Pb with $(6s)^2$ valence electron configuration tend to lose inversion symmetry due to mixing with the $(6s)^1(6p)^1$ excited state where the lowering of the total energy is bigger than that caused by the bringing back to the centrosymmetric site by overcoming the Coulomb repulsion. Therefore, the stereochemical activity of a lone-pair in Pb-6*s* combines with the off-centre of Ti to provide more switchable paths in the new structure, and makes it a potential magnetoelectric material.[12]

Table 4. BEC tensor $Z^\star$ for ions in Pb_2TiVO_6.

$Z^\star$	xx	yy	zz
Pb	3.671	3.671	3.558
Ti	5.779	5.779	4.941
V	4.635	4.635	4.313
O1	–2.326	–2.326	–3.795
O2	–2.490	–4.752	–1.716

4. Conclusion

Motivated by our previous work in which a magnetoelectic material is predicted by doping Ti in its parent material $BiFeO_3$, we predicted a new material by means of partial substitution of V by Ti in $PbVO_3$ across the *ab* plane. The hypothetical Pb_2TiVO_6 is calculated to have a good insulating property in AFM spin configuration with a band gap of 1.45 eV using the LSDA+U scheme. The magnetic moment of 1 μ_B in one unit cell mainly comes from the non-bonding orbital d_{xy} in a majority spin channel. Based on the modern theory of polarization, an electric polarization of 42.67 $\mu C/cm^2$ is evaluated using the Berry-phase method. The lone-pair of Pb-6*s* and the off-centring of Ti and V can provide the possibility of the reorientation of polarization in the hypothetical structure.

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