Prediction of Magnetoelectric behavior in Bi$_2$MnTiO$_6$

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Abstract. We present results from ab initio calculations based on density functional theory for bismuth-based double perovskite Bi$_2$MnTiO$_6$. Using total energy calculation with stress and force minimization we have predicted the equilibrium crystal structure for Bi$_2$MnTiO$_6$ considering potential structures into the calculation. We have predicted that the ground state of Bi$_2$MnTiO$_6$ will be a noncentrosymmetric rhombohedral structure with space group R3c. Our spin polarized calculation for different possible collinear magnetic configurations we found that Bi$_2$MnTiO$_6$ will be an insulator with G-type antiferromagnetic ordering in its ground state. The coexistence of both stereochemically active Bi-6s lone pair and the Ti$^{4+}$ with $d^0$-ness which bring covalency results in the stabilization of noncentrosymmetric structure and thus ferroelectricity. Our orbital projected density of states plot shows that the Mn$^{4+}$ in Bi$_2$MnTiO$_6$ will be at high spin state with a spin moment of 4.28 $\mu_B$. Hence Bi$_2$MnTiO$_6$ is predicted to be a magnetoelectric material.

Keywords: Magnetoelectrics, Multiferroics.

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INTRODUCTION

There has been growing interest in multiferroic materials due to the coupled magnetic, electric and/or structural order parameters which result in (anti)ferromagnetic, (anti)ferroelectric and/or ferroelastic properties in the same phase. Due to these combinations, the magnetic properties can be manipulated by applying either electric or magnetic field. Bi based multiferroics have become a center of attraction due to high value of electric polarization and Bi$^{3+}$ is more environment friendly than Pb$^{2+}$. In addition, the stereochemical activity of Bi$^{3+}$ is being exploited in magnetic oxides, with the goal of forming ferromagnetic-ferroelectric coupling. BiMnO$_3$ undergoes monoclinic to monoclinic transition at 474 K and monoclinic to orthorhombic transition at 770 K. Montanari et al. found that below 770 K BiMnO$_3$ has a centrosymmetric $C2/c$ space group by neutron powder diffraction experiments. Since the $C2/c$ structure of BiMnO$_3$ has inversion symmetry, the net electric polarization is zero. The mechanism of breaking the inversion symmetry with magnetism was considered recently in ref. 8. It was found that the peculiar orbital ordering was realized below 474 K gives rise to ferromagnetic interactions between nearest-neighbor spins which compete with longer-range antiferromagnetic interaction. Solovyev and Pchelkina predicted that $C2/c$ symmetry in BiMnO$_3$ is spontaneously broken by hidden AFM interactions, which lowers the actual symmetry to the $Cc$ space group which allows for the existence of both ferromagnetic order and ferroelectric polarization. The Ti doping in BiMnO$_3$ is expected to increase the magnetoelectric coupling in Bi$_2$MnTiO$_6$ as the $d^0$-ness of Ti$^{4+}$ will give rise to off center displacement to the system. However, there is no theoretical prediction has been done for this compound with Ti doping up to now. This motivated the present study.

COMPUTATIONAL DETAILS

The present calculations were performed using the Vienna ab-initio simulation package (VASP) within the projected augmented plane wave (PAW) method together with the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) for the exchange correlation potential. A very large basis set of 800 eV for the plane wave cut off was used in order to reproduce the structural parameters correctly. Structural optimizations were continued until the forces on the atoms had converged to less than 1 meV/Å and the pressure on the cell had minimized within the constraint of constant volume. 6x6x6 k-
The curve for C121 is not shown here because its energy is very high as compared to the energy for the ground state configuration R3.

mesh was used for R3 structure and similar k-point density has been used for all the other potential structures considered here. In order to identify the correct magnetic ground state, we have considered non-magnetic (NM), ferromagnetic (FM) and three antiferromagnetic (AFM) configurations such as A, C, G-AF configurations. The Born effective charges (BEC) are calculated for the ground state configuration using the so called "Berry phase finite difference approach" in which the electronic contribution to the change of polarization is estimated using modern theory of polarization.

RESULTS AND DISCUSSIONS

For the study of structural phase stability, we have considered six closely related potential structure types: tetragonal Amm2, cubic Fm-3m, tetragonal P4mm, rhombohedral R3, monoclinic C121, and monoclinic C2/c (Fig. 2). The structures were fully relaxed for all volumes considered in the present study using force as well as stress minimization. From Fig. 2 it is clear that the noncentrosymmetric rhombohedral R3 (space group 146) structure is energetically lower among the structural configurations considered here. The calculated volume vs total energy curve was fitted to Murnaghan equation of states to get equilibrium volume, bulk modulus and its pressure derivative. The optimized equilibrium structural parameters are as follows: Volume (V) = 129.70 Å³, a = 5.69 Å, α = 59.80 and the positions of the atoms are Bi (1a) (0.000/0.507), Mn/Ti (1a) (0.233/0.729), O1 (3a) (0.568, 0.926, 0.388) and O2 (3a) (0.882, 0.454, 0.037). The equilibrium bulk modulus and its pressure derivative obtained from the fitting are 80.7 GPa and 6.34 respectively. It may be noted that the equilibrium structure obtained for Bi2MnTiO6 is closely related to the R3c structure found experimentally and

FIGURE 1. Crystal structure of Bi2MnTiO6 in the R3 structure. Highly distorted MnO6 and TiO6 octahedras are corner shared through oxygen. Also note that Bi atoms are not present in the middle between the octahedras owing to the displacement of Bi due to the presence of 6s lone pair electrons.

FIGURE 2. Calculated cell volume vs total energy for antiferromagnetic Bi2MnTiO6 in different structural arrangements (structure types being labeled on the illustration).

FIGURE 3. Calculated orbital-projected density of states of Mn2+ (left) and Ti4+ (right) for Bi2MnTiO6 in the ground state G-AFM configuration.

*The curve for C121 is not shown here because its energy is very high as compared to the energy for the ground state configuration R3.*
TABLE I. Calculated Born effective charge for antiferromagnetic Bi₂MnTiO₆

| Z   | Position | xx    | yy    | zz    | xy    | xz    | yx    | yz    | zx    | zy    |
|-----|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Bi  | 1a       | 5.177 | 4.999 | 4.380 | -0.505| -0.241| 0.049 | -0.688| -0.573| 4.380 |
| Bi  | 1a       | 4.565 | 4.592 | 4.670 | 0.127 | 0.004 | -0.062| 0.129 | 0.105 | 4.670 |
| Mn  | 1a       | 2.886 | 2.788 | 2.500 | -0.048| -0.212| -0.167| -0.240| -0.152| 2.500 |
| Mn  | 1b       | 5.593 | 5.482 | 5.128 | 0.204 | -0.495| -0.505| -0.193| -0.045| 5.128 |
| O   | 3b       | -2.742| -3.243| -2.692| -0.635| -0.141| -0.409| 0.422 | -0.532| -2.692|
| O   | 3b       | -3.115| -2.831| -2.681| -0.329| 0.746 | 0.008 | -0.402| 0.576 | -2.681|

The curve for C121 is not shown here because its energy is very high as compared to the energy for the ground state configuration R3

theoretically for BiFeO₃ and to the R3 structure predicted theoretically for Bi₂FeTiO₆.

Our calculations show that the magnetic ground state of Bi₂MnTiO₆ will be G-AFM. The calculated total energies with respect to ground state G-AFM configuration for ferromagnetic, A-AFM, C-AFM and nonmagnetic states are 7 meV, 477 meV, 476 meV and 1851 meV/f.u., respectively. The integrated spin density at the Mn site is found to be 4.28 µB/Mn atom. This clearly indicates that Mn2+ ion in Bi₂MnTiO₆ is in HS state and also our BEC shows strong covalent interaction between transition metal and oxygen. The stabilization of ferroelectric phase is originating from the lone pair electron at the Bi³⁺ site and covalency from Ti⁴⁺ ion.

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REFERENCES

1. J.F. Scott, Nat. Mater. 6. 256 (2007).
2. P. Ravindran, R. Vidya, A. Jekshus, H. Fjellvåg, and O. Eriksson, Phys. Rev. B 74, 224412 (2006).
3. P. Ravindran, R. Vidya, O. Eriksson, and H. Fjellvåg, Adv. Mater. 20, 1353 (2008).
4. E. Montanari, G. Calestani, A. Migliori, M. Dapiaggi, F. Bolzoni, R. Cabassi, and E. Gilioli, Chem. Mater. 17, 6457 (2005).
5. A. Moreira dos Santos, A.K. Cheetham, T. Atou, Y. Syono, Y. Yamaguchi, K. Ohoyama, H. Chiba, and C.N.R. Rao, Phys. Rev. B 66, 064425 (2002).
6. T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Syono, J. Solid State Chem. 145, 639 (1999).
7. E. Montanari, G. Calestani, L. Righi, E. Gilioli, F. Bolzoni, K.S. Knight, and P.G. Radaelli, Phys. Rev. B - Condens. Matter Mater. Phys. 75, 1 (2007).
8. I. V. Solovyev and Z. V. Pchelkina, New J. Phys. 10, (2008).
9. I. V. Solovyev and Z. V. Pchelkina, New J. Phys. 10, (2008).
10. G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6. 15 (1996).
11. G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
12. P.E. Blochl, Phys. Rev. B 50, 17953 (1994).
13. J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
14. P. Ravindran, A. Jekshus, H. Fjellvåg, A. Delin, and O. Eriksson, Phys. Rev. B 65, 064445 (2002).
15. R. Resta, Rev. Mod. Phys. 66, 899 (1994).
16. C. Michel, J.-M. Moreau, G.D. Achenbach, R. Gerson, and W.J. James, Solid State Commun. 7, 701 (1969).
17. H.J. Feng and F.M. Liu, Phys. Lett. Sect. A Gen. At. Solid State Phys. 372, 1904 (2008).