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Theoretical investigations of structural and magnetic ground state stability of BiMnO₃

Sathya Sheela Subramanian, Chinathambi Kanagaraj and Baskaran Natesan¹

National Institute of Technology, Tiruchirapalli, 620015, India

Abstract

We investigate the crystal structure and magnetic ground state of monoclinic BiMnO₃ using first principles calculations, in order to shed some light on the long standing issues related to the structural stability and ferroelectric polarization of BiMnO₃. Our total energy calculations based on full structural optimization reveals that BiMnO₃ stabilizes to monoclinic C2/c (centrosymmetric) with ferromagnetic ground state. Furthermore, to validate model calculations report, in which antiferromagnetic ordering is assumed to co-exist with ferromagnetism, to drive ferroelectric polarization, we invoke antiferromagnetic ordering in our calculations and find that this ordering indeed breaks the inversion symmetry and induces ferroelectric polarization along *x-z* plane.

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1. Introduction

Multiferroics are an interesting class of materials which exhibit both magnetic and ferroelectric properties in the same phase. This leads to the possibility of controlling the magnetic order by the application of electric field and electric order by the application of magnetic field, paving ways for potential applications of these materials in the areas of information storages and magnetic sensors as noted by Kimura et al. (2003), Ederer et al. (2004), Khomskii (2007) and Cheong et al. (2006). Multiferroics are basically classified into two types, namely type I and type II. In type I, the ferroelectric polarization (*P*) originates from the displacement of ions due to lattice distortions as suggested by Khomskii (2009), and is found to be very large. But the coupling between the ferroic orders is weak. On the contrary, in type II, *P* arises due to certain magnetic ordering and is electronic in origin, see, Sergienko et al. (2006). Even though, in type II, *P* is found to be much less than that of type I, the coupling between the two ferroic orders is better than that of type I. Among type I multiferroics, BiFeO₃ is a well studied material exhibiting a very large *P*. In BiFeO₃, *P* is driven by the structural distortion caused by the stereochemical activity of the Bi 6s² lone pairs as reported by Wang et al. (2006) and Ravindran et al. (2006). Similar kind of polarization mechanism was predicted by Hill et al. (1999) from their first principle studies carried out on monoclinic BiMnO₃ with *C2* symmetry, which was later confirmed by experimental investigations carried out by Atou et al. (1999) and Moreira dos Santos et al. (2002). However, recently, Belik et al. (2007) and Montanari et al. (2007) have shown from their electron and neutron diffraction studies that BiMnO₃ crystallizes in a centrosymmetric monoclinic *C2/c* structure with a ferromagnetic ordering. This is consistent with the theoretical reports of Baettig et al. (2007), wherein, full structural optimization of monoclinic *C2* structure is shown to crystallize to *C2/c* structure with less energy. These results in turn raises further questions regarding the ferroelectric behavior of BiMnO₃, as the centrosymmetric *C2/c* structure do not

* Corresponding author. Tel.: 91-431-2503606; fax: 91-431-2500133.
E-mail address: nbaski@nitt.edu

allow ferroelectric polarization. Recently, Solovyev et al. (2009, 2010) using model Hamiltonian calculations have demonstrated the possibility of hidden antiferromagnetic (AFM) ordering together with ferromagnetic ordering in centrosymmetric $C2/c$ structure. They further argued that this hidden AFM ordering breaks the inversion symmetry and leads to the development of small amount of P which is electronic in nature and originates from exchange-striction driven mechanism proposed by Picozzi et al. (2007, 2008), similar to that predicted in orthorhombic (o) RMnO_3 ($R=\text{Ho-Lu}$) by Sergienko et al. (2006).

Thus, motivated by the controversies surrounding the structural stability and multiferroic behavior of monoclinic BiMnO_3 , we carry out first principle density functional theory (DFT) calculations under generalized gradient approximation (GGA), in order to better understand the structural stability and ferroelectric polarization of BiMnO_3 . We also invoke AFM spin ordering in the $C2/c$ structure to validate the model calculation predictions which suggest that certain kind of hidden AFM ordering is necessary to induce ferroelectric polarisation in this structure.

2. Computational Details

The structural optimization of monoclinic BiMnO_3 with $C2$ and $C2/c$ structures for different magnetic configurations such as A-AFM, C-AFM, G-AFM and FM were carried out using plane wave pseudo potential method implementations of DFT using ABINIT by Gonze et al. (2002, 2005, 2009) within the GGA by including the onsite coulomb interaction $U-J = 5$ eV. The magnetic ordering of A-AFM, C-AFM and G-AFM structures is taken using the standard classification scheme proposed by Wollan et al. (1955). In the plane wave method, an optimized $4 \times 4 \times 4$ Monkhorst pack grid and an energy cut-off of 40 Hartree was used. Calculations were carried out under Perdew-Burke-Ernzerhof parameterization of GGA using PBE potential (for Bi, Mn O) derived by Perdew et al. (1996). The structural optimization was done using the Broyden-Fletcher-Goldfarb-Shannon minimization algorithm. The structures have been relaxed in the self-consistent calculations by restricting the total energy differences not exceeding 10^{-5} eV, along with stringent force cut-off conditions in the self-consistent iterations. Electric polarization calculations were done using the Berry phase (BP) method of King-smith (1993) and Resta (1992).

3. Results and Discussion

In order to determine the structural stability and ferroelectric nature of monoclinic BiMnO_3 , we carried out full structural optimization of non-centrosymmetric $C2$ and centrosymmetric $C2/c$ structures using GGA+U method of DFT. We used experimental lattice parameters of Belik et al. (2007), and Atou et al. (1999) and dos Santos et al. (2002) as starting configurations for $C2/c$ and $C2$ structures, respectively. The optimization of these structures was performed under different collinear magnetic orderings such as A-AFM, C-AFM, G-AFM and FM. The total energies obtained after full structural optimization for these structures are listed in Table 1.

Table 1. The total energies (meV/Mn) of optimized $C2/c$ and $C2$ phases of BiMnO_3 .

Phase	$C2/c$	$C2$ (Atou's)	$C2$ (Santo's)
A-AFM	43.7	47.1	55.8
C-AFM	80.8	84.6	93.0
G-AFM	112.1	116.0	124.5
FM	0.0	11.8	11.8

It is noted from Table 1 that, consistent with recent experimental studies by Belik et al. (2007) and Montanari et al. (2007) and theoretical studies by Baettig et al. (2007), our results further confirms that the ferromagnetic $C2/c$ is the most stable magnetic ground state structure of monoclinic BiMnO_3 . The difference between our results and Baettig et al (2007) is that the present calculations were done with GGA+U formalism of DFT, besides carrying out the full structural optimization for A-AFM, C-AFM, G-AFM and FM orderings to get the true magnetic ground state. Furthermore, it is also observed that the optimization of Atou's and dos Santos $C2$ experimental structures converge to the same final structure, but the symmetry does not change as reported by

Baettig et al. (2007). We attribute this to the difference in the functionals employed in GGA over LDA calculations of Battig et al. (2007). It is also noted that the GGA is known to give much better accuracy over LDA in manganite containing systems.

We show in Fig. 1 and 2, respectively, the optimized crystal structures of $C2/c$ and $C2$ space group in the most stable magnetic ground state (FM). The lattice parameters and atomic positions for optimized $C2/c$, $C2$ (Atous's) and $C2$ (Santos's) structures are listed in Table 2 and 3, respectively. It is evident from Fig. 1 and 2 that both $C2/c$ and $C2$ structures possess elongated MnO_6 octahedra revealing highly distorted nature of $BiMnO_3$ perovskite. This strong distortion of MnO_6 octahedra can be related to certain orbital ordering which favours the observed FM ordering of both $C2/c$ and $C2$ structures.

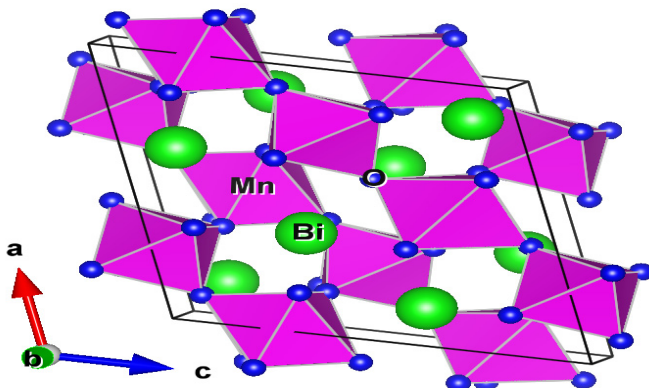


Fig. 1. Optimized crystal structure of $BiMnO_3$ with $C2/c$ symmetry.

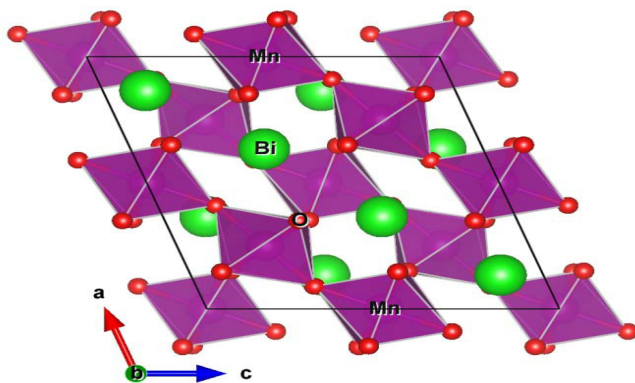


Fig. 2. Optimized crystal structure of $BiMnO_3$ with $C2$ symmetry.

Table 2: Lattice parameters of optimized C2/c, C2 (Atou's) and C2 (Santo's) structures.

Phase	C2/c	C2 (Atou's)	C2 (Santo's)
a (Å)	9.550	9.546	9.546
b (Å)	5.618	5.614	5.613
c (Å)	9.872	9.867	9.864
α (°)	90.0	90.0	90.0
β (°)	110.7	110.7	110.6
γ (°)	90.0	90.0	90.0

Table 3. Optimized atomic positions for C2/c, C2 (Atou's) and C2 (Santo's) structures.

Atom	Site	x	y	z
C2/c				
Bi	8f	0.1345	0.2280	0.1215
Mn1	4e	0.0000	0.2126	0.7500
Mn2	4d	0.2500	0.2500	0.5000
O1	8f	0.0942	0.1764	0.5799
O2	8f	0.1471	0.5654	0.3756
O3	8f	0.3502	0.5438	0.1656
C2 (Atous)				
Bi1	4c	0.1345	0.0514	0.3718
Bi2	4c	0.3657	0.0953	0.1281
Mn1	2a	0.0000	0.0367	0.0000
Mn2	4c	0.2499	0.0731	0.7499
Mn3	2b	0.5000	0.1097	0.5000
O1	4c	0.0939	0.0002	0.8300
O2	4c	0.4059	0.1462	0.6699
O3	4c	0.1472	0.3874	0.6252
O4	4c	0.3503	0.3665	0.4154
O5	4c	0.3504	0.2588	0.1254
O6	4c	0.1473	0.2588	0.1253
C2 (Santos)				
Bi1	4c	0.1344	0.0160	0.3719
Bi2	4c	0.3655	0.0604	0.1278
Mn1	2a	0.0000	0.0023	0.0000
Mn2	4c	0.2499	0.0384	0.7499
Mn3	2b	0.5000	0.0743	0.5000
O1	4c	0.0940	0.9655	0.8300
O2	4c	0.4061	0.1110	0.6700
O3	4c	0.1472	0.3521	0.6251
O4	4c	0.3504	0.3314	0.4153
O5	4c	0.3504	0.2453	0.9153
O6	4c	0.1472	0.2246	0.1250

Since, symmetry constraints do not allow ferroelectric polarization in the stable C2/c centrosymmetric structure of BiMnO₃; we invoke an inversion symmetry breaking collinear AFM order and evaluate polarization after optimizing the structure. We consider the following two AFM configurations on the Mn spins of BiMnO₃ by invoking symmetry operations of the C2/c group, combined with time-inversion symmetry as proposed by Solovyev et al. (2009, 2010): (i) "↑↑↓↓" and (ii) "↑↓↑↑". The direction of magnetic moments for these two AFM orderings was chosen as suggested by Solovyev et al. (2009, 2010). In "↑↑↓↓" AFM configuration, we found that the centrosymmetry of the structure was intact and thus there is no net polarization. While, the other AFM configuration, "↑↓↑↑", seems to break the inversion symmetry of C2/c and changes the symmetry to P2 leading to the emergence of polarization of 0.8 μC/cm² along x-axis and 0.2 μC/cm² along z-axis. Therefore, the observed ferroelectric behavior is attributed to the magnetic ordering induced symmetry breaking effect. Thus our finding supports the view of Solovyev et al. (2009, 2010) that the possible driving force for the observation of polarization in this system could be due to certain kind of hidden AFM ordering. Furthermore, on contrast to large polarization reported in C2 structure which originates from the structural distortion caused by the off-centering displacement of lone pair (Bi) ions, the emergence of small polarization observed in C2/c structure could be attributed to the exchange striction mechanism as observed in orthorhombic RMnO₃ series by Sergienko et al. (2006).

4. Conclusion

We conclude from our first principles calculations that centrosymmetric C2/c is the most stable crystal structure of monoclinic BiMnO₃ with FM as magnetic ground state, possessing no net polarization. Therefore, we invoke "↑↓↑↑" AFM ordering in the C2/c structure to validate model Hamiltonian predictions. Our results, consistent with model calculation reports, show that the center of symmetry (inversion symmetry of C2/c) is broken when the Mn spins are aligned to "↑↓↑↑" AFM state, and this leads to the development of small polarization in the x-z plane.

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