

Tb_{0.5}Bi_{0.5}MnO₃: New material. A DFT study

Miguel Grizalez^{a,b,c,*}, M. Jairo Arbey Rodríguez^d, Jesús Heiras^e, P. Prieto^{a,b}

^aGrupo de Películas Delgadas, Universidad del Valle, Colombia

^bCentro de Excelencia en Nuevos Materiales, Cali, Valle, Colombia

^cUniversidad de la Amazonia, Florencia, Caquetá, Colombia

^dGEMA–Grupo de Estudio de Materiales, Universidad Nacional de Colombia, Bogotá, Colombia

^eCentro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, UNAM, Ensenada, BC, México

Available online 12 September 2007

Abstract

In the present work we have determined the band structure and the densities of states (DOS) of Tb_{0.5}Bi_{0.5}MnO₃ in cubic phase using the density functional theory (DFT). The determination of the lattice constant was made by minimizing the energy as a function of volume. The internal coordinate of the O-atom was optimized. From these optimizations we have found that the lattice constant is 8.482 Å and the bond length between Tb and O-atoms is 2.193 Å and the one for Bi and O-atoms is 2.051 Å. From a study of the DOS of *f*-Tb, e_g and t_{2g}-Mn atomic-like orbitals for each spin polarization we conclude that there exists a permanent magnetic moment of about 16 Bohr magneton per unit cell. Also, a metallic behavior is displayed, and thus it is expected that ferroelectricity will disappear. Inside the conduction band, next to Fermi level, two peaks in the DOS-spin-down are observed, which are due to *f*-Tb. Therefore, conduction electrons will be spin-down polarized and this shows that Tb_{0.5}Bi_{0.5}MnO₃ has possible applications in spintronics.

© 2007 Elsevier Ltd. All rights reserved.

PACS: 61.50.-f; 62.20.-x; 75.20.En; 71.15.Nc; 71.20.-b; 71.55.Ht

Keywords: Mechanical and structural properties; DFT; Band structure; Density of states; Magnetic properties; Tb_{1-x}Bi_xMnO₃

1. Introduction

Multiferroics are materials which exhibit simultaneously at least two of the “ferro” properties such as ferromagnetism, ferroelectricity and ferroelasticity in a given range of temperatures [1]. Magnetoelectrics, a kind of multiferroic materials, show a spontaneous magnetization and electrical polarization that can be reoriented applying an electric field or magnetic field, respectively. As a consequence of these states, they suggest many applications that include multiple-state memory elements, transducers, actuators and storage devices.

Tb_{0.5}Bi_{0.5}MnO₃ is a single-phase multiferroic which exhibits only one crystalline structure. The TbMnO₃ crystallizes in orthorhombic structure whereas the BiMnO₃ displays polymorphism according to temperature.

It is known that it is ferromagnetic with a triclinic structural distortion in its ground state. Calculations have been made in cubic phase using tight binding [2] and from the results it can be concluded that it shows a metallic behavior.

It is known that TbMnO₃ is a multiferroic that exhibits ferroelectric properties at about 30 K and magnetic characteristics at ~40 K [3]. More recently, Golovenchits and Sanina [4] presented the semiconductor Tb_{0.95}Bi_{0.05}MnO_{3+0.005} which due to nonstoichiometry in oxygen gave rise to the appearance of electron charge carriers. As a result, the material is a strongly compensated semiconductor. Tb_{1-x}Bi_xMnO₃ for *x* ≤ 0.2 seems to be insulator or semiconductor, and presents the perovskite structure, (Pbnm space group).

In this work we concentrate our attention in a material that is possibly magnetoelectric multiferroic, which is simultaneously ferromagnetic and ferroelectric, with or without ferroelasticity. Then our interest in the Tb_{1-x}Bi_xMnO₃ for *x* = 0.5 is related to its magnetic and electronics properties. The study, we present here, is based on the density functional

*Corresponding author. Grupo de Películas Delgadas, Universidad del Valle, Colombia. Fax: +57 1 316 5135.

E-mail address: mgrizales@calima.univalle.edu.co (M. Grizalez).

theory (DFT) [5,6]. Calculations were carried out with the wien2k code [7] in cubic perovskite structure.

2. Method used and Calculation details

The calculations were carried out with DFT within Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) [8]. The wien2k code [7] was used in order to obtain the structural and electronics properties. The crystalline structure is showed in Fig. 1 and the atomic positions are presented at Table 1.

The space group used is #225 ($Fm\bar{3}m$) with four chemical formulas within a unit cell. The muffin-tin radius for Tb, Mn, Bi and O atoms were 1.04, 0.98, 1.19 and 0.85 Å, respectively. Other parameters of wien2k were $RMT \times K = 7.00$, $G_{max} = 14.00$ and maximum angular momentum inside the muffin-tin sphere $l = 10$. A mesh $12 \times 12 \times 12$ over the irreducible Brillouin zone (BZ), which produces 72 inequivalent k -points, was used. Spin polarized was taken in account in calculations. In order to obtain the best volume, energy versus volume was plotted, and the Murnaghan's equation [12] was used to fit the data. At the minimum the density of states (DOS) was calculated.

3. Results and discussion

Fig. 2 shows the variation of energy as a function of volume. From the fitting to the Murnaghan's equation, the minimum energy is obtained for 1029.686 Bohr³, which implies a lattice constant $a = 16.030 \text{ Bohr} = 8.482 \text{ \AA}$ and the bulk modulus $B_0 = 118.6 \text{ GPa}$. Fig. 2 was calculated within spin polarized.

Fig. 3 shows the DOS for each spin orientation. The dashed-line is the reference energy which is the Fermi level. At left of the figure, in the valence band, we observe that

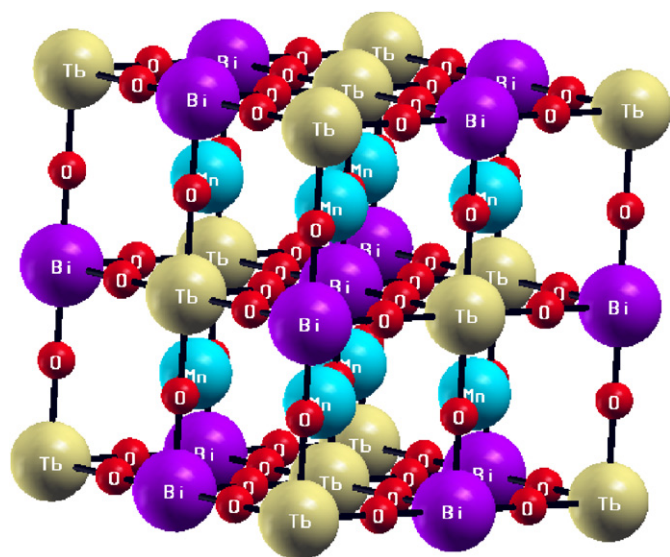


Fig. 1. Perovskite structure used in calculations of properties of $Tb_{1-x}Bi_xMnO_3$ $x = 0.5$ [9–11].

Table 1
Position in crystal coordinates for the elements of $Tb_{0.5}Bi_{0.5}MnO_3$

| Element | Position | |
|---------|---|---|
| Tb | (0, 0, 0) | |
| Bi | ($\frac{1}{2}$, 0, 0) | |
| Mn | ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) | |
| O | (u , 0, 0) | ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) |
| | (0, u , 0) | (1 - u , 0, 0) |
| | (0, 0, u) | (0, 1 - u , 0) |
| | | (0, 0, 1 - u) |

The internal parameter u was optimized and its best value is 0.2582.

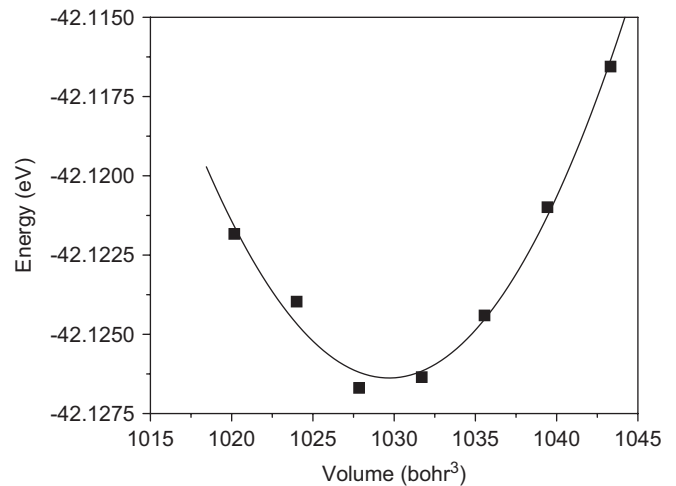


Fig. 2. Energy as a function of volume for $Tb_{0.5}Bi_{0.5}MnO_3$. The least-square fit to the Murnaghan's state equation is shown as solid line [12]. The volume in plot is the volume by each chemical formula.

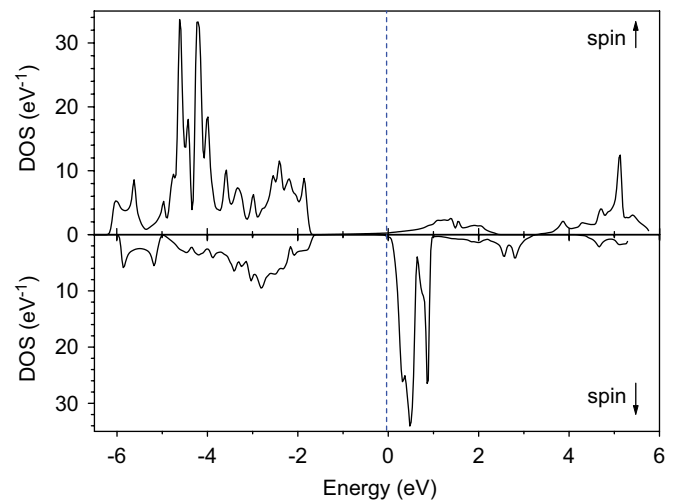


Fig. 3. Density of states (DOS) for the $Tb_{0.5}Bi_{0.5}MnO_3$. The upper-half and the bottom-half correspond to the spin up and spin down polarization, respectively. Reference of energy is the Fermi level.

the DOS for spin up and spin down are no symmetric and the difference between them produces a total magnetic moment of approximately $16 \mu_B$. That permanent magnetic

moment is due to f -Tb as well as e_g and t_{2g} -Mn atomic-like orbitals. The Fermi level is at the bottom of the conduction band suggesting that the material possibly exhibits a metallic behavior. At right of the figure, in the conduction band, next to Fermi level we observe two peaks in the DOS-spin-down which is due to f -Tb. Therefore, the conduction electrons will be spin-down polarized. This fact shows that $Tb_{0.5}Bi_{0.5}MnO_3$ has a possible application in spintronics.

4. Conclusions

In this work we have found the main features of the structure, electronics and magnetic properties of the $Tb_{0.5}Bi_{0.5}MnO_3$. The theoretical method used was the DFT theory with the Perdew–Burke–Ernzerhof GGA approximation. The method used to solve the Khon–Sham equations was the FP-LAPW as it is implemented in the wien2k program. In the structural study we have optimized the volume of unit cell and the internal coordinate of the O-atom. We have found that the lattice constant is 8.482 Å and the bond lengths between Tb and O- and Bi and O-atoms are 2.193 and 2.051 Å, respectively. Also, we conclude that there exists a permanent magnetic moment of about $16\mu_B$ per unit cell. Additionally, it displays metallic behavior and thus it is expected that ferroelectricity will disappear, due to the existence of a total DOS of f -Tb atomic-like orbitals next to the Fermi level in the conduction band. The conduction electrons will be spin-down polarized implying that the material has potential application in spintronics. In a near future, the predictions

we have done in this theoretical paper will be investigated experimentally using $Tb_{0.5}Bi_{0.5}MnO_3$ in bulk and thin films. The thin films will be deposited using RF magnetron sputtering method.

Acknowledgments

The Excellence Center for Novel Materials, the Universidad Nacional (DIB) and Proy. PAPIIT No. IN114207 support this work. Special thanks to Dr. Peter Blaha for his help.

References

- [1] H. Schmid, *Ferroelectrics* 162 (1994) 317–338.
- [2] N. Hill, *J. Phys. Chem. B* 104 (29) (2000) 6694–6709.
- [3] T. Kimura, T. Goto, H. Shintani, et al., *Nature* 426 (2003) 55.
- [4] E.I. Golovenchits, V.A. Sanina, *J. Exp. Theor. Phys. Lett.* 81 (10) (2005) 509–513.
- [5] P. Hohenberg, W. Khon, *Phys. Rev.* 136 (3B) (1964) B864.
- [6] W. Khon, L.S. Sham, *Phys. Rev.* 140 (4A) (1965) A1133.
- [7] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Aug-mented Plane Wave+Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Universität Wien, Austria (2001), ISBN 3-9501031-1-2.
- [8] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (18) (1996) 3865.
- [9] A. Kokalj, *Comp. Mat. Sci.* 28 (2003) 155–168.
- [10] A. Kokalj, *J. Mol. Graphics Modelling* 17 (1999) 176–179.
- [11] A. Kokalj, M. Causà, *Proceedings of High Performance Graphics Systems and Applications European Workshop, Bologna, Italy, 2000*, pp. 51–54.
- [12] F.D. Murnaghan, *Proc. Natl. Acad. Sci. USA* 30 (1994) 244.