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Journal of Magnetism and Magnetic Materials 320 (2008) e85–e87

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# Structural and magnetic properties of double-perovskite $\text{Ba}_2\text{MnMoO}_6$ by density functional theory

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Available online 20 February 2008

## Abstract

Perovskite-like materials which include magnetic elements have relevance due to the technological perspectives in the spintronics industry. In this work, we report the studies of  $\text{Ba}_2\text{MnMoO}_6$  material by using the density functional theory. The interchange-correlation potential was included through the generalized gradient approximation. Our structural calculations are in agreement with the experimental results which show that the material crystallizes in the 225 space group ( $\text{Fm}\bar{3}\text{m}$ ) and has a lattice parameter of about 8070 Å. The density of states study was carried out by considering the up and down spin orientations. Results show that  $\text{Ba}_2\text{MnMoO}_6$  has a conductor behavior due to dominant Mn spin-up and Mo spin-down contributions. The magnetic moment was calculated to be  $2.9 \mu_{\text{B}}$ .

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Keywords: Electronic structure; DFT; Complex perovskite

## 1. Introduction

Physical properties of perovskite-like ceramics are particularly sensible to inhomogeneities like distortions from the ideal cubic structure of the  $\text{ABO}_3$  formula, vacancies and chemical substitutions [1]. One of these anomalies, which raises the complex perovskite with  $\text{A}_2\text{BB}'\text{O}_6$  formula, results from the ordering of B and B' cations on the octahedral site of the primitive perovskite unit cell. The importance of complex perovskites is in the possibility of creating new magnetic materials  $\text{A}_2\text{BB}'\text{O}_6$ , with A being an alkaline earth ion and B, B' being transition metal ions. Recently, the study of these materials has increased due to the possibility of applying them in the design and technology of magnetic memories, tunnel junctions and other magnetic devices in the novel spintronics area [2].

With the objective of theoretically determining the physical effects in the chemical composition of the material due to the inclusion of magnetic elements, in this work

we developed an *ab initio* exhaustive study of a double perovskite with  $\text{A} = \text{Ba}$ ,  $\text{B} = \text{Mn}$  and  $\text{B}' = \text{Mo}$ . This material was recently synthesized but its magnetic and structural properties lack a detailed theoretical study [3].

## 2. Calculation method

We use the Wien2k [4] which is a program based on the density functional theory (DFT) [5,6] and that allows to perform electronic structure calculations of crystalline solids. Wien2k works with the full-potential (linearized) augmented plane-wave (LAPW)+local orbital (lo) method, which is most accurate for band structure calculations. The exchange correlation potential can be treated using several approximations in the framework of the local density approximation (LDA) and the generalized gradient approximation (GGA) [7]. By searching the energy minimum, we have optimized the unitary cell volume and the  $x$  parameter. From the volume, the lattice parameter  $a$  is easily found. The muffin-tin radii used, in Å, were 2.50, 1.99, 1.99 and 1.77 for Ba, Mn, Mo and O, respectively.  $\text{RMTK}_{\text{max}} = 8.0$ . We used 120  $k$ -points over the irreducible Brillouin zone and the maximum angular momentum

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inside the muffin-tin sphere is  $l = 10$ . Magnetic character of the system was introduced by the spin polarization into the GGA. From the energy-volume DFT calculations, we determined the optimal structure for the  $\text{Ba}_2\text{MnMoO}_6$  system using the  $\text{Fm}\bar{3}\text{m}$  (2 2 5) space group. The unitary cell volume and  $x$  parameter were optimized by searching the energy minimum. The lattice parameter  $a$  was easily found from the calculated volume.

### 3. Results and discussion

Fig. 1 shows the energy as a function of volume. Each one of the squared points constitutes an individual calculation and the line corresponds to a fitting with the Murnaghan's state equation, which was carried out by using the concept of the least-square fitting method [8,9] which is 98.3% in agreement with the experimental report,  $a = 8.207 \text{ \AA}$  [3], and 99% with the structure prediction diagnostic software SPuDS,  $a = 7.982 \text{ \AA}$  [10]. The bond length Mn–O is  $2.074 \text{ \AA}$  and the bond length Mo–O is  $1.961 \text{ \AA}$ , which reveals that O is closer to Mo. These values are in accordance with the experimentally reported Mn–O and Mo–O bond distances ( $2.158$  and  $1.926 \text{ \AA}$ ) [3].

Fig. 2 shows the density of states (DOS) as a function of energy for the lattice constant obtained from Fig. 1. Fermi level is the reference for the energies. From the total DOS (Fig. 2a), it is observed that for both spin-up and spin-down orientations this material exhibits a conductor character, e.g., no half-metallic behavior is evidenced.

Particularly, the metallic feature can be attributed to the dominant spin-up contributions of Mn and spin-down of Mo. Partial DOS for Mn and Mo are shown in Fig. 2b and c. Below the Fermi level, which corresponds to zero energy, we determine a dominant spin-up contribution of Mn to the magnetic moment of  $\text{Ba}_2\text{MnMoO}_6$  material.

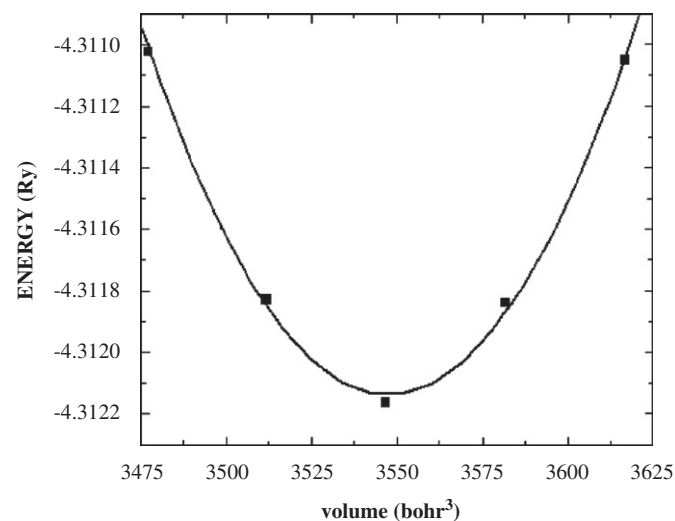


Fig. 1. Squared points represent the calculated data of energy as a function of volume for the primitive cell of  $\text{Ba}_2\text{MnMoO}_6$ . Line corresponds to the fitting with the Murnaghan's state equation by the least-square method.

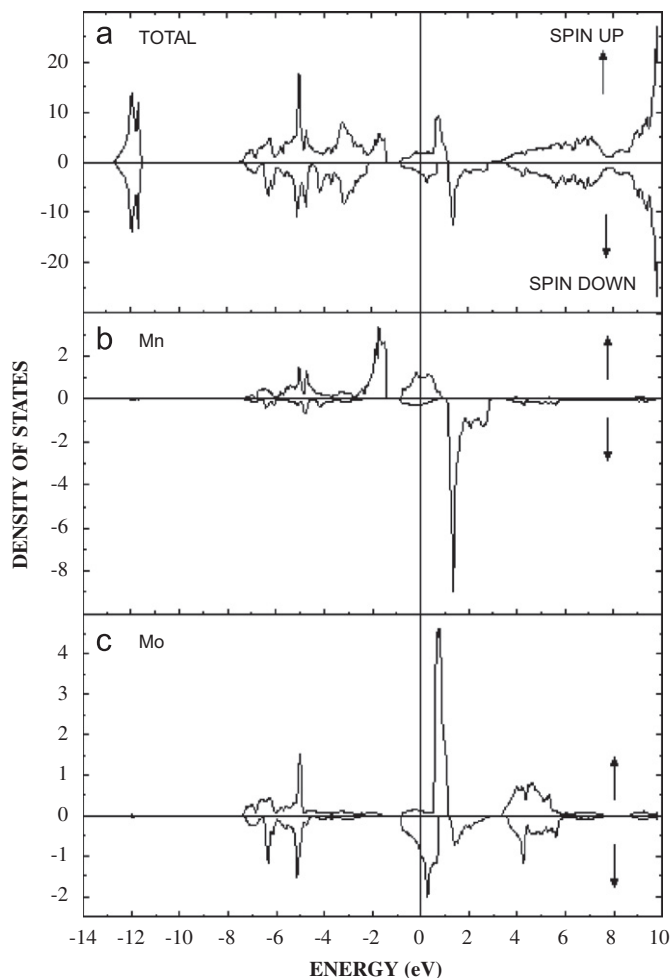


Fig. 2. Calculated total and partial (Mn, Mo) DOS of  $\text{Ba}_2\text{MnMoO}_6$  for up and down spin polarizations. In the figure, positive DOS represents spin up and negative DOS spin down.

The calculated value is  $3.8 \mu_B$ , which corresponds to 65.5% of the reported experimental result  $5.8 \mu_B$  [3]. This disagreement could be because we do not take into account the minority contribution of Mn- $e_g$  orbital and the incipient effect of Mo- $e_g$  orbital to the magnetic moment.

As shown in Fig. 3, we calculated the DOS for the  $t_{2g}$  and  $e_g$  electrons for both Mn and Mo elements. It is clear from Fig. 3 that while the orbital Mn- $t_{2g}$  (spin up) is directly responsible for the magnetic response, orbitals Mn- $e_g$  (up orientation) and Mo- $t_{2g}$  (spin down) evidence the majority contribution to the conductor character of the  $\text{Ba}_2\text{MnMoO}_6$  material. However, incipient participation of orbitals Mo- $e_g$  (spin up) and Mn- $t_{2g}$  (spin down) to the conductor feature of the system is observed. On the other hand, in order to guarantee the availability of despairing Mo d-orbital for the existence of an effective magnetic moment, and from our results, we suggest the appropriated valences  $\text{Mn}^{3+}$  and  $\text{Mo}^{5+}$  instead of  $\text{Mn}^{2+}$  and  $\text{Mo}^{6+}$ , as proposed in Ref. [3]. Fig. 3 clearly shows the superposition of the partial DOS for localized Mn- $t_{2g}$  and delocalized Mn- $e_g$  levels, which characterize the splitting of the crystalline field between  $t_{2g}$  and  $e_g$  states [11] from 1.2 up

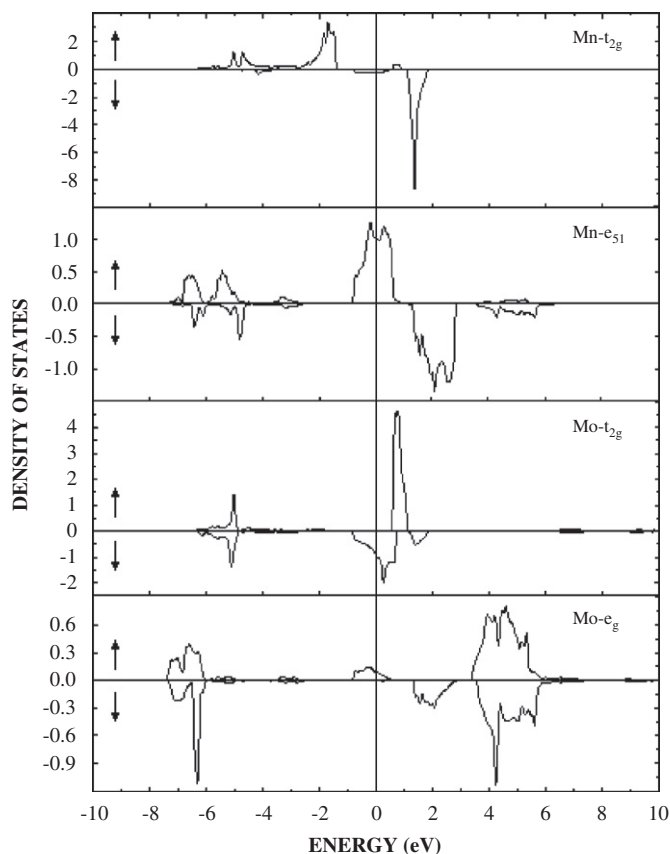


Fig. 3. Contribution of  $t_{2g}$  and  $e_g$  electrons to the DOS for up and down spin polarizations calculated for  $\text{Ba}_2\text{MnMoO}_6$ . In the figure, positive DOS represents spin up and negative DOS spin down.

to 1.8 eV, and for Mo- $t_{2g}$  and Mo- $e_g$  from 1.5 up to 1.9 eV. Exchange splitting occurring between  $t_{2g}$  up and  $t_{2g}$  down levels and between  $e_g$  up and  $e_g$  down levels is observed for Mn- $t_{2g}$  (−1.4 up to 1.2 eV), Mn- $e_g$  (0.7 up to 1.4 eV) and Mo- $e_g$  (0.5 up to 1.3 eV).

#### 4. Conclusions

DFT calculations of the structural parameters of the  $\text{Ba}_2\text{MnMoO}_6$  perovskite were performed by considering

the  $\text{Fm}\bar{3}m$  space group. The theoretical lattice parameter is  $a = 8.070 \text{ \AA}$ , which differs around 1.7% as compared with the experimental reported value [3]. The bulk modulus is  $\sim 95 \text{ GPa}$  but experimental reports of this parameter do not exist. The DFT calculations predict that  $\text{Ba}_2\text{MnMoO}_6$  material has a metallic feature. The one responsible for this conductor character is the dominant contributions to the DOS of Mn-spin up and Mo-spin down. We attributed the magnetic moment as a result of the predominant contribution of Mn- $t_{2g}$  orbital. Effects of exchange splitting and crystalline field splitting were observed from the DOS of localized and delocalized  $t_{2g}$  and  $e_g$  states.

#### Acknowledgments

This work was partially supported by the COLCIENCIAS Colombian agency on the project No. 1101-06-17622 and contract 043-2005 of Centro de Excelencia en Nuevos Materiales. The authors wish to thank Dr. Peter Blaha for special support.

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