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# Rietveld refinement and electronic structure studies for the $\text{Sm}_2\text{FeMnO}_6$ new complex perovskite

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## Abstract

We report synthesis and crystalline structure study of the  $\text{Sm}_2\text{FeMnO}_6$  new complex perovskite, by X-ray diffraction experiments and through the application of Rietveld refinement. Results revealed the crystallization of system in a structure given by Pmn21 (#31) space group and lattice parameters  $a = 7.621(1) \text{ \AA}$ ,  $b = 5.675(3) \text{ \AA}$  and  $c = 5.378(3) \text{ \AA}$ . *Ab initio* calculations of density of states (DOS) and electronic structure were carried out for this perovskite-like system by the density functional theory (DFT) and using the full-potential linearized augmented plane waves (FP-LAPW) method. All calculations were carried out using spin polarization. Material evidences a conductor-like character, predominantly due to  $d_{-xy}$  Fe orbital of the spin down channel. Magnetic response of system has contributions of Fe and Mn spin up orientation. The calculated magnetic moment in cell was  $34.48 \mu_B$  and the magnetic moment in interstitial was  $1.54 \mu_B$ . © 2008 Elsevier B.V. All rights reserved.

**Keywords:** New complex perovskite; Electronic structure; DFT

## 1. Introduction

Ceramic materials represent a great percentage of systems, which are currently investigated by the physics, and chemistry of solids. Particularly, the perovskite family has concentrated important attention in last decades. From the point of view of chemical composition, perovskites have characterized by the ideal formula  $\text{ABX}_3$ , where A generally is an alkaline earth element, B represents a transition metal element and X, more of times, is the oxygen. Modifications of atomic radii of A and B, introduce structural distortions and new crystalline phases. Inclusions of rare earth elements replacing the alkaline earth in the A site, and magnetic elements in the B site, give the possibility to produce materials with exotic electric and magnetic properties [1,2]. When B cation is 50% substituted, the  $\text{A}_2\text{BB}'\text{O}_6$  complex perovskite is created. Its chemical configuration supplies multiple chances to combine different elements of periodic table, generating the possibility to synthesize new materials, which involve a larger gamma of physical properties.

Sometimes, it is possible to combine diverse properties in a same material, as is the case of multiferroic perovskites, which evidence the coexistence of ferromagnetic and ferroelectric ordering [3]. This circumstance provides an additional degree of freedom to control magnetic devices from electric fields and vice versa [4]. Another exotic behavior of double perovskites is the spin polarization effect observed in half-metallic materials, which simultaneously show insulator and conductor electric response for the up and down spin channels [5]. We think could be possible that more of half-metallic complex perovskite must to present multiferroic behavior. In the last years, density functional theory (DFT) has constituted in a strong tool to predict half-metallic [5] and multiferroic [6] materials. In this report we present results of DFT calculations for the new perovskite-like material  $\text{Sm}_2\text{FeMnO}_6$ . We synthesize the material and initialize DFT calculations from the experimental crystallographic parameters.

## 2. Experimental

Samples of  $\text{Sm}_2\text{FeMnO}_6$  were synthesized by means the standard solid-state reaction method. Precursor powders

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Table 1  
Atomic positions of  $\text{Sm}_2\text{FeMnO}_6$  obtained from Rietveld analysis

Atom	x	y	z
Sm	0.7500	0.2500	0.0125
	0.7500	0.7500	0.5125
	0.2500	0.2500	0.0125
	0.2500	0.7500	0.5125
Fe	0.0000	0.1957	0.5250
	0.5000	0.8043	0.0250
Mn	0.5000	0.3043	0.5000
	0.0000	0.6957	0.0000

Position of oxygen atoms are shown in Fig. 1(a).

were stoichiometrically mixed according to the chemical formula. Each of these mixtures was ground to form a pellet. Samples were annealed and sintered for 48 h at 1450 °C. The XRD pattern of this powder material was recorded by means of Phillips PW1710 diffractometer ( $\lambda = 1.5406 \text{ \AA}$ ). We perform measurements in the  $2\theta$  interval between 15° and 85°, with a scanning step of 0.02° and 2 s exposure time. Rietveld refinement of this pattern was carried out by means of the GSAS code [7]. Table 1 shows results of Rietveld refinement for orthorhombic space group Pmn21.

### 3. Calculation method

Calculations of electronic structure for the complex perovskite  $\text{Sm}_2\text{FeMnO}_6$  were performed by employing the full-potential linearized augmented plane waves (FP-LAPW) method to solution the Kohn–Sham equations, in the framework of DFT and as implemented in the wien2k code [8,9]. The exchange and correlation effects were treated by using the generalized gradient approximation (GGA) [10]. The self-consistent calculations are considered to be convergent when the total energies of two successive iterations agreed within  $10^{-4}$  Ry. We adjusted the Fermi energy to zero. The calculation was performed using the space group #31 (Pmn21), with the lattice parameters  $a = 7.6211 \text{ \AA}$ ,  $b = 5.6753 \text{ \AA}$  and  $c = 5.3783 \text{ \AA}$  (Fig. 1a). The exchange–correlation potential was approximate using the Perdew–Burke–Ernzerhof-96 model [10]. The maximum momentum angular used was 10. For integrations we utilized 60  $k$ -points in the irreducible first Brillouin zone, which is showed in Fig. 1(b), and the  $\text{RMT} \times K_{\text{max}}$  was 8. These two last values were selected from a several graphs of energy vs.  $k$ -points for  $\text{RMT} \times K_{\text{max}} = 7.0, 7.5, 8.0$  and  $8.5$  as parameter. The values were chosen as those in which the variation of the energy was equal or less than 0.0001 Ry. The muffin-tin radii were 1.0531, 1.1536, 0.9314 and 1.1536 Å for Sm, Mn, O and Fe, respectively.

### 4. Results and discussion

Fig. 2 shows results of total density of states (DOS) for both spin up and down polarizations.

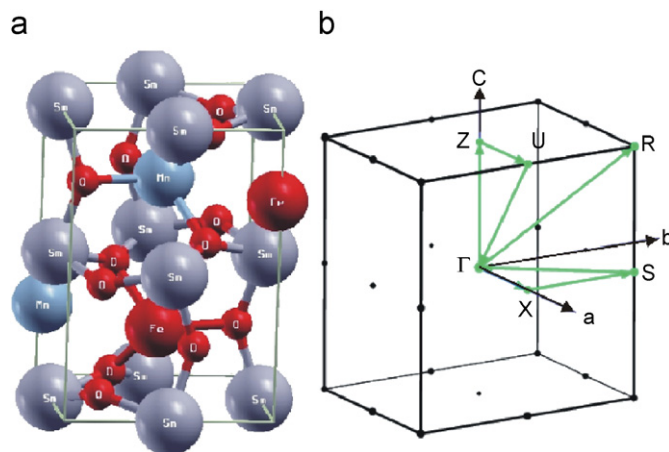


Fig. 1. (a) Crystalline structure of  $\text{Sm}_2\text{FeMnO}_6$  perovskite material and (b) first Brillouin zone and high symmetry points, which were used in DFT calculations.

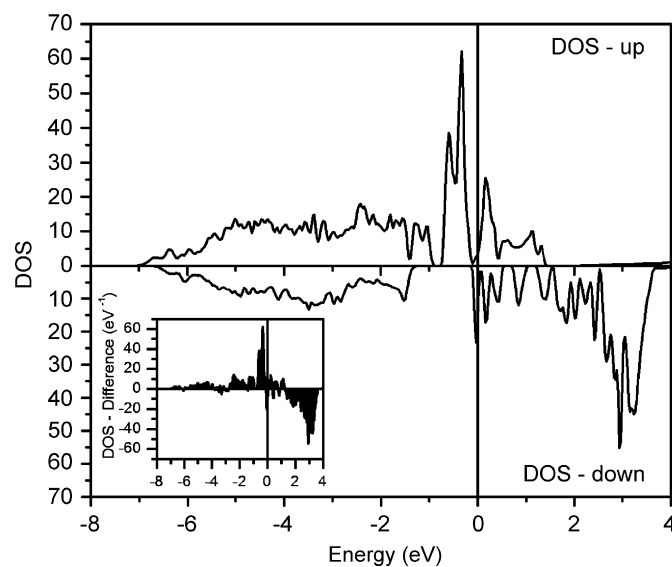


Fig. 2. Total DOS of  $\text{Sm}_2\text{FeMnO}_6$  calculated for up (above) and down (below) spin configurations. Inset shows the difference between spin up and spin down DOS.

The Fermi level is the reference for energy. In the inset the difference between the DOS for spin up and spin down channels is shown. The first observation is that the material exhibits metallic-like behavior. In the range between  $-0.8$  and  $0 \text{ eV}$  we observe that the DOS for spin up orientation is dominant, but at the Fermi level and above the spin down has main contribution.

Fig. 3 presents the partial DOS for Fe and Mn with spin polarization. We observe that below the Fermi level spin up for both Fe and Mn are predominant. Above the Fermi level, spin down contributions of Fe and Mn are observed. However, the predominant contribution to the conductor character is attributed to spin down Fe, which has a continuous behavior through the Fermi level (from  $-0.05$  up to  $0.8 \text{ eV}$ , approximately).

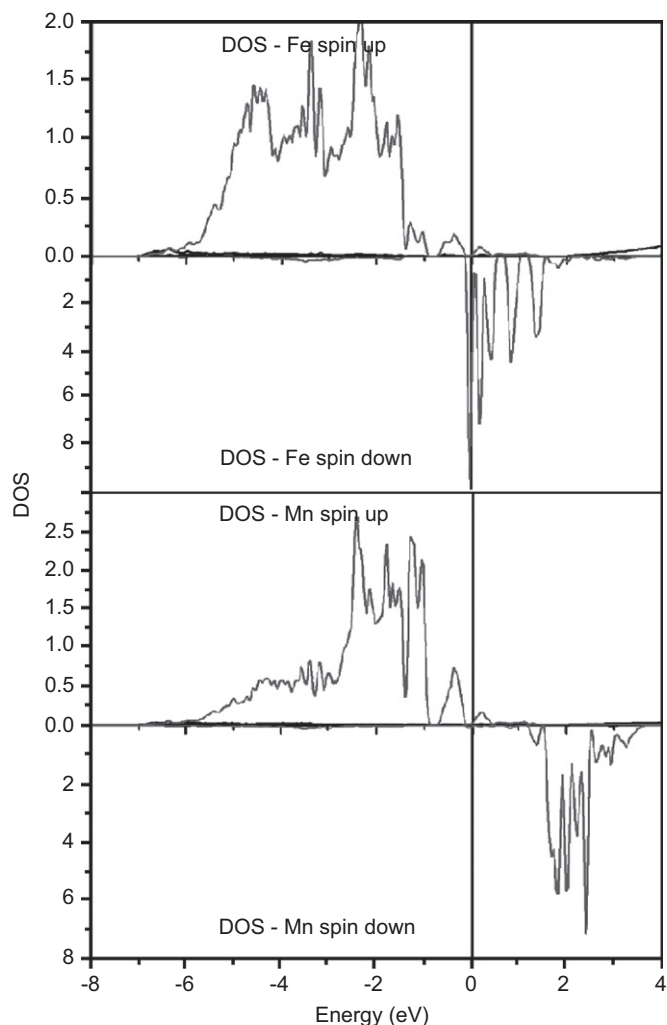


Fig. 3. Partial Fe and Mn contributions to DOS calculated for up and down spin configurations.

On the other hand, magnetic characteristic of system arises from the spin up polarization of Fe and Mn. Magnetic moments of mixed charge density were calculated. Total magnetic moment in cell was determined to be  $34.48 \mu_B$  and the magnetic moment in interstitial was  $1.54 \mu_B$ . Partial DOS calculated for the d-Fe and d-Mn orbital permit to conclude that the magnetic moment has main contributions from  $xy$  and  $z^2$  orbital of spin up Fe, and  $xz$  and  $z^2$  orbital of spin up Mn.

## 5. Conclusions

$\text{Sm}_2\text{FeMnO}_6$  complex perovskite was synthesized by solid-state reaction method. Structural characterization was carried out by XRD and Rietveld refinement method showed that the material crystallized in an orthorhombic structure, space group  $\text{Pmn}21$ , with the lattice parameters  $a = 7.6211 \text{ \AA}$ ,  $b = 5.6753 \text{ \AA}$  and  $c = 5.3783 \text{ \AA}$ . From these results DFT calculations were initialized, considering spin polarization. Material evidences a conductor-like character, predominantly due to d- $xy$  Fe orbital of the spin down channel. Magnetic response of the system has contributions of Fe and Mn spin up orientation.

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