



# Effect of the transition metal ratio on bulk and thin slab double perovskite $\text{Sr}_2\text{FeMoO}_6$



J. Pilo<sup>a</sup>, A. Trejo<sup>a</sup>, E. Carvajal<sup>a,\*</sup>, R. Oviedo-Roa<sup>b</sup>, M. Cruz-Irisson<sup>a</sup>, O. Navarro<sup>c</sup>

<sup>a</sup> Instituto Politécnico Nacional, ESIME-Culhuacán, Av. Santa Ana 1000, México, D.F. C.P. 04430, Mexico

<sup>b</sup> Instituto Mexicano del Petróleo, Lázaro Cárdenas 152, México, D.F. C.P. 07730, Mexico

<sup>c</sup> Unidad Morelia del Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Antigua carretera a Pátzcuaro 8701, Col. Ex. Hda. de Sn. José de la Huerta, C.P. 58190 Morelia, Michoacán, Mexico

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## ABSTRACT

Double perovskites are promising materials for multiple applications on microelectronics, specially on magnetic devices development. Perhaps the most interesting one is the double perovskite  $\text{Sr}_2\text{FeMoO}_6$  since its magnetic properties differ from that of other related simple perovskites:  $\text{SrFeO}_3$  and  $\text{SrMoO}_3$ . In this work the evolution of the electronic properties and the magnetic moment distribution as a function of the Fe/Mo ratio in bulk and a thin slab of  $\text{Sr}_2\text{FeMoO}_6$  was studied. The thin slab was constructed keeping free surfaces parallel to the (001) crystalline planes with different thickness and compositions. All calculations were made in the Density Functional Theory scheme in the Generalized Gradient Approximation, using the Perdew-Burke-Ernzerhof functional, as implemented in the DMol<sup>3</sup> code. After being geometry optimized, the electronic Density of States and band structure were calculated, as well as the magnetic moment distribution, for each modeled system. Essential results are as follows: for the bulk cases it was found that half-metallic behavior which characterizes the stoichiometric double perovskite changes if the compound becomes molybdenum or iron rich; for the slab is remarkable the induction of magnetic moments, owed to the corresponding to iron atoms, over their neighbor atoms.

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## 1. Introduction

The double perovskite  $\text{Sr}_2\text{FeMoO}_6$  (SFMO) is an interesting material which has colossal magnetoresistive behavior and high Curie temperature ( $T_c \sim 420$  K), reported by Kobayashi et al. [1], making it suitable for potential microelectronic applications as memory devices; additionally, SFMO thin films have been studied in the recent years, showing promising results for the development of magnetoelectronic devices [2–6]. Spintronics is the most interesting among the possible applications of SFMO, owing to their half-metallic behavior, which could be used for magnetic tunnel junctions; however, to implement these applications is of great importance to get control on the electronic properties of the SFMO slab systems. It has been observed that the SFMO properties depend on the relative concentration and order of the transition metals, thus the large tunneling magnetoresistive values could be tuned by changing such concentrations [7–11]. Another mechanism to control the properties of SFMO comes from quantum confinement: as measurements on synthesized SFMO thin films show, its physical properties change compared to the bulk SFMO [4,12,13]; however, those experiments were made on polycrystalline samples and the associated data

reflect the consequential behavior of having multiple orientations of single crystals.

There have been multiple investigations on SFMO. For instance, on previous works the disorder and magnetic transitions on were studied by means of a tight-binding model and the renormalized perturbation expansion technique [14–19], where due to computational limitations a comparison between the calculated electronic properties and those reported from experiment was not possible. On the other hand, the first attempts to study SFMO in the DFT scheme involved antisite occupation in the bulk and the smallest clusters made up by the transition metals and the oxygen atoms which surround them [20,21]; however, the theoretical characterization of SFMO thin films and the variations of its electronic properties, related to the transition metal concentration, have not been studied theoretically in full detail (at the best of our knowledge), without ignoring the multiple focused reports as those from Zhang et al. [22,23]. Motivated by the experimental evidence, in this work the electronic properties of thin films of SFMO double perovskite were studied as a function of the transition metals content ratio; this is the basis for a systematic and detailed study which must include the increasing thickness of the slab, the metals content ratio and the interaction among neighboring slabs including the supporting material. Results show that, with great concentrations of either Fe or Mo the system has a metallic behavior, while the SFMO film has half metallic

\* Corresponding author.

E-mail address: [ecarvajalq@ipn.mx](mailto:ecarvajalq@ipn.mx) (E. Carvajal).

properties. These results could be important for the potential applications of SFMO in spintronics.

**2. Model and computational method**

From a bulk crystalline SFMO (modeled after experimental data:  $I4/mmm$  spatial group and lattice parameters  $a = 5.5711 \text{ \AA}$  and  $c = 7.9000 \text{ \AA}$  [24]) a thin slab was excised with free surfaces parallel to the  $\{001\}$  crystalline planes. Due to periodic conditions the slab was placed on a supercell so that the distance between the slab and its replica is about  $10 \text{ \AA}$  along the  $[001]$  direction (Fig. 1). To analyze the different concentrations two more slab systems were developed: SFO (Fe rich slab) and SMO (Mo rich slab). These slabs were achieved by modifying the bulk crystalline model, which corresponds to the appropriate simple perovskite. The electronic properties of the SFMO slabs were calculated within the Density Functional Theory (DFT) scheme, using the Generalized Gradient Approximation and the Perdew–Burke–Ernzerhof functional [25], as implemented in the DMol<sup>3</sup> code, where the slabs undergo a geometry optimization process to identify their minimum energy configurations. The convergence criteria were  $2 \times 10^{-5} \text{ Ha}$ ,  $4 \times 10^{-3} \text{ Ha/\AA}$  and  $5 \times 10^{-3} \text{ \AA}$  tolerances for the energy change, the gradient and the maximum displacement, respectively; we used  $4 \times 4 \times 1$  k-point mesh, based on preliminary calculations on ultrathin slabs, where it was observed that adding k-points to the calculations do not reduce significantly the total energy.

**3. Results and discussion**

The systematic study started modeling ultrathin slabs (half the bulk parameter wide) for which, however, the convergence of the geometry optimization was impossible calculations. Besides, previous experiences show that the computational cost increases if the on-site Coulomb repulsive energy is taken into account, without changing the qualitative behavior; also, previous works about perovskite-type clusters revealed that the isolation of octahedral oxygen coordinated transition metals produces a decoupling of their electronic states hybridizations [21], hence a slab with the full  $c$  bulk crystalline parameter was chosen to perform the subsequent calculations. The lattice parameters for the three slab systems (SFMO, SFO and SMO) change slightly, once the conventional cells geometry was optimized, with SFO showing the biggest change (Table 1) of around 8%. From the calculated densities of states (Figs. 2–5) it is possible to see that SMO and SFO bulk systems have no band gap energy thus behave like metals, without spin polarization in the former and spin polarized in the latter, while the SFMO thin slab preserves the half metallic behavior which characterizes the associated bulk system [1,20]; nevertheless, the magnitude of the energy band gap increases slightly (0.975 eV) compared to bulk SFMO (0.952 eV from our calculations). Meanwhile, the SMO and SFO thin slab systems are conductors, being the DOS comparable for both spin channels near the Fermi level (Figs. 4, 5), with the occupied states

**Table 1**

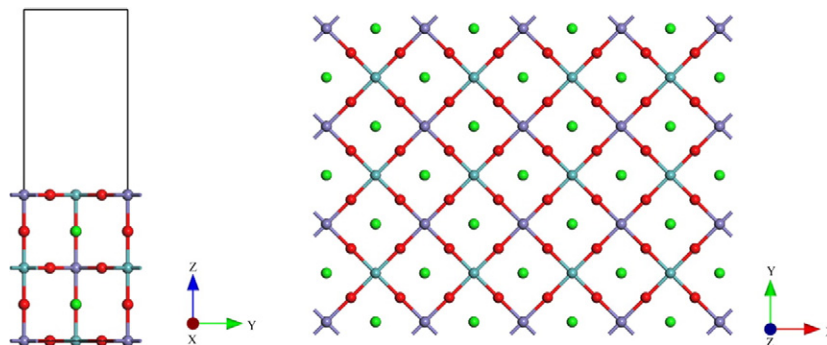
Cell parameter values for the modeled bulk and thin slab for each system.  $a$ ,  $b$  and  $c$  stand for optimized bulk cell parameters. The initial cell parameters (before geometry optimization) were  $a = b = 5.57 \text{ \AA}$  and  $c = 7.88 \text{ \AA}$  for all slabs while  $a_1$ ,  $b_1$  and  $c_1$  denote the final cell parameter values, after the geometry optimization calculations. The energy for each slab system is shown at the right end column of the table.

Perovskite system	Bulk cell parameter $a = b$ (Å)	Bulk cell parameter $c$ (Å)	Slab cell parameter $a_1 = b_1$ (Å)	Slab cell parameter $c_1$ (Å)	Slab system energy (eV)
SFMO	5.730	8.101	5.552	7.903	−801,611.62
SMO	4.063	4.078	5.648	7.940	−1,023,149.01
SFO	3.939	3.940	5.125	8.176	−580,069.26

numbers differing for each spin channel. The spin polarization is inexistent in the bulk  $\text{SrMoO}_3$  (Fig. 2); however, the confinement induces a differentiation on the energy associated to the electronic states of each spin channel (Fig. 4), by keeping similar bands and states distribution on the energy interval. On the other hand, the confinement induces a clearly metallic behavior on both spin (polarized) channels of the  $\text{SrFeO}_3$  slab.

This performance must be linked to the magnetic behavior of the atomic species set, mainly the transition metals. As considered for diverse models, bulk SFMO physical characteristics are due to the spin values on the Fe and Mo sites: the spin configuration of ions is  $3d^5 S = 5/2$  for  $\text{Fe}^{3+}$  and  $4d^1 S = 1/2$  for  $\text{Mo}^{5+}$ ; if the magnetic arrangement between  $\text{Fe}^{3+}$  and  $\text{Mo}^{5+}$  ions is considered, the bulk SFMO is ferrimagnetic and the ideal saturation magnetic moment is  $4 \mu_B$  [1–4,8, 10–12,24]. The current results show that, the magnetic moment values obtained for the SFMO slab system align parallel to each other; the higher value is associated to the central Mo atom and is even bigger than the one corresponding to the Fe atoms, which reach the highest value if the atom is at the surface of the slab (Table 2). The magnetic behavior for the SMO slab system is similar: magnetic moments are aligned in a ferromagnetic way and the superior values are associated to the Mo atoms which are on the surface. On the contrary, the magnetic moments in the SFO slab system arrange in a ferrimagnetic way, the smallest values are associated to the atoms at the surface while the inner Fe atoms achieve the highest moment values among all the atoms of the three systems. However, by contrasting the results obtained for these slabs, it seems that the increase of the Mo content leads to a better ferromagnetic slab.

Diverse reported experimental results associate a smaller (than the ideal) magnetization value for  $\text{Sr}_2\text{FeMoO}_6$ , for bulk or film samples; for the latter, typically one fourth of the ideal value [2]. Also, the  $\text{Sr}_2\text{FeMoO}_6$  magnetization value depends on the substrate where the film was deposited. To support SFMO films on  $\text{SrTiO}_3$  could reduce the magnetization magnitude, but the use of MgO even could make it unmeasurable [5]. Then, the chemical complexity of these perovskite compounds and their sensitivities to the crystalline orientation and kind of supporting substrate [6] are elements, among others, that evidence



**Fig. 1.** Lateral (left) and top (right) views of a SFMO double perovskite thin slab. The red, blue, green and purple spheres represent O, Mo, Sr and Fe atoms, respectively. Each axis system is an aid to the scheme at its left.

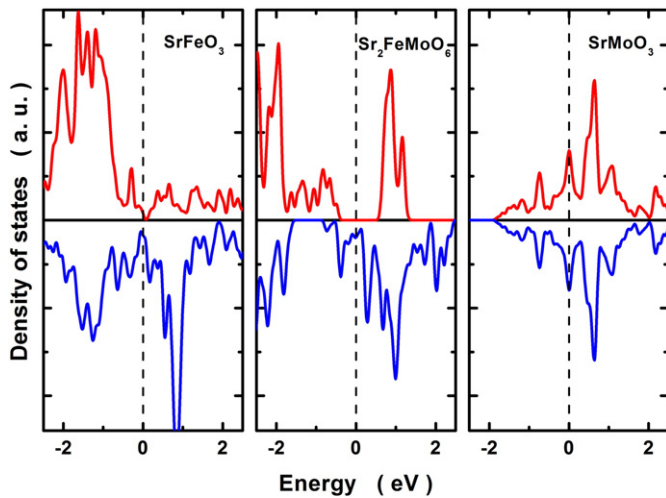


Fig. 2. Density of states for the SrMoO<sub>3</sub>, Sr<sub>2</sub>FeMoO<sub>6</sub> and SrFeO<sub>3</sub> bulk perovskites, from left to right. Curves in blue correspond to the down-spin channel while curves in red correspond to the up-spin channel. The black vertical dashed line indicates the Fermi level.

the necessity of a systematical study of these perovskite films as a function of their thickness and the supporting substrate at least. On this scenario, the obtained results cannot be compared to experimental reported data, because many of the latter are associated to (111) epitaxial films grown on Ba<sub>0.4</sub>Sr<sub>0.6</sub>TiO<sub>3</sub> or SrTiO<sub>3</sub> substrates and all of these samples have a thickness which is one order of magnitude larger than the modeled slabs [12]. Even when perovskite thin films are deposited on single-crystalline (mostly (001) SrTiO<sub>3</sub>) or polycrystalline substrates the common factor is the film thickness, typically around few hundred nanometers [4,26,27]. Having synthesized films where the average grain size for SFMO is a hundred times thicker than our model, the Asano's group identified an insulating barrier which associates to the surface oxygen excess because they could not identify it from XPS data, without being conclusive [12]. From our model results, this behavior must be related to the energy gap for one of the spin channels.

Because there are reports on the dependence between the electrical behavior and the film deposition temperature, whose authors agree about the necessity that thin films must be well fabricated and

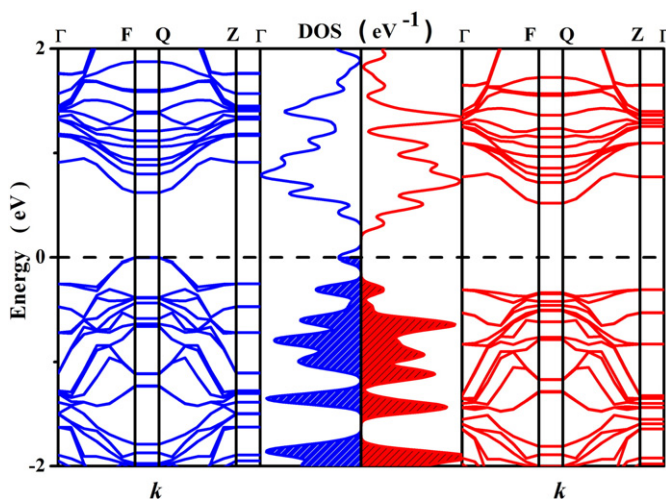


Fig. 3. Electronic band structure and density of states for the Sr<sub>2</sub>FeMoO<sub>6</sub> double perovskite slab. Curves in blue (at the left) correspond to the down-spin channel while curves in red (at the right) correspond to the up-spin channel. The black horizontal dashed line indicates the Fermi level and the central filled graphs indicate the occupied states.

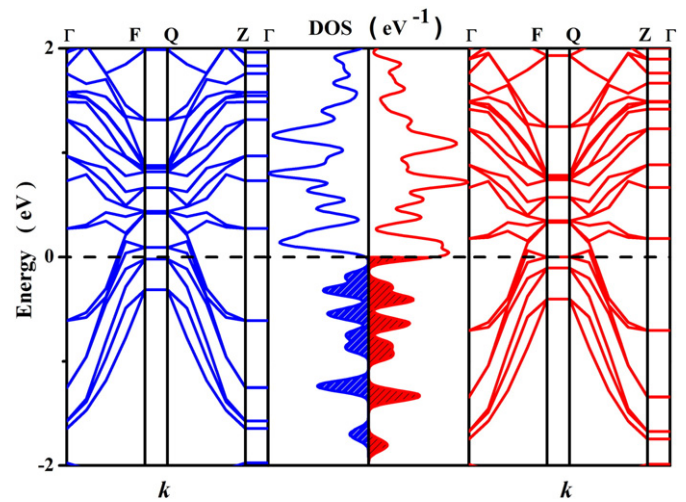


Fig. 4. Electronic band structure and density of states for the SrMoO<sub>3</sub> perovskite slab. Curves in blue (at the left) correspond to the down-spin channel while curves in red (two at the right) correspond to the up-spin channel. The black horizontal dashed line indicates the Fermi level and the central filled graphs indicate the occupied states.

characterized to be used in spintronics applications, Shinde et al. [4] studied the magneto-transport properties of SFMO films on SrTiO<sub>3</sub> (STO) substrates. They found that Fe—Mo ordering only occurs if the film was deposited at high temperatures on (001) STO substrate, but dissociates to form SFO and SMO clusters above 1000 °C. These results are relevant because their magnetization measurements involve smaller values for films deposited at lower temperatures, fact which agrees with our result for the SFMO thin slab: it splits between the metallic and the semiconducting behaviors, one for each spin channel. Besides, our results for the SFO slab (metallic and ferrimagnetic behaviors) agree with the low temperature measurements made on 20 and 30 nm thick SFO films, for which tensile strain, oxygen deficiency and temperature can modify their physical properties [28,29]. Comparing the results from our calculations against experimental measurements on SMO films grown on (001) STO substrates [27,30] there is a coincidence about the conducting behavior and the contribution on it from

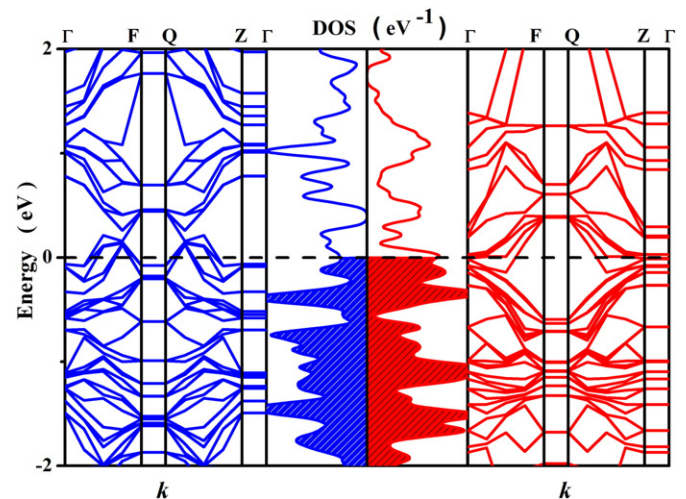
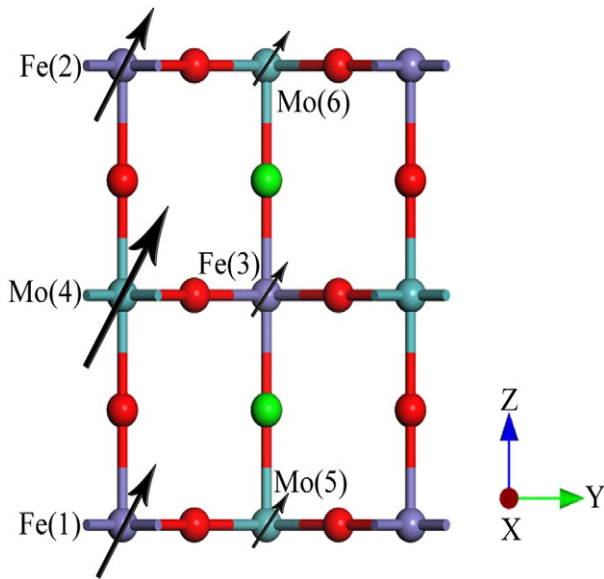


Fig. 5. Electronic band structure and density of states for the SrFeO<sub>3</sub> perovskite slab. Curves in blue (at the left) correspond to the down-spin channel while curves in red (at the right) correspond to the up-spin channel. The black horizontal dashed line indicates the Fermi level and the central filled graphs indicate the occupied states.



**Fig. 6.** Magnetic moments orientation for the SFMO slab. The black arrows show the relative moment orientations; the Fe and Mo tags, (1–3) and (4–6) respectively, are to indicate where Fe and Mo atoms are placed in the supercell. The same sequence is followed to indicate where the metallic atoms are placed in the SFO and SMO cells.

**Table 2**  
Magnetic moment values for transition metal atoms in each thin slab system model. The position of each transition metal (tagged by numbers) atom is shown in Fig. 6. Minus signs indicate the opposite relative moment orientation.

Sr <sub>2</sub> FeMoO <sub>6</sub>		SrMoO <sub>3</sub>		SrFeO <sub>3</sub>	
Atom	Mag. moment (h)	Atom	Mag. moment (h)	Atom	Mag. moment (h)
Fe(1)	0.194	Mo(1)	0.182	Fe(1)	−0.367
Fe(2)	0.194	Mo(2)	0.182	Fe(2)	−0.367
Fe(3)	0.016	Mo(3)	0.088	Fe(3)	1.063
Mo(4)	0.255	Mo(4)	0.088	Fe(4)	1.063
Mo(5)	0.042	Mo(5)	0.182	Fe(5)	−0.367
Mo(6)	0.042	Mo(6)	0.182	Fe(6)	−0.367

the 4d Mo electrons. Some differences are the bigger cell parameter values for our model and even the magnetic behavior that could be paramagnetic for the bulk SMO.

In addition, spintronics applications usually require systems built up by stacking films which interact among them [31–33], modifying the behavior which would show if would be isolated. For different perovskites, there are reports about the change of the magnetic behavior related to one of the two parts that conform a system, owed to the interaction among these parts; such is the case of the interaction through exchange bias of the LaNiO<sub>3</sub> (LNO) and LaMnO<sub>3</sub> (LMO) perovskites. The stoichiometric bulk LMO is a Mott insulator; however, grown as a thin film, LMO typically exhibits a ferromagnetic behavior. For epitaxial grown LNO and LMO superlattices an onset of magnetization was observed, depending on temperature and the number of unit cells of each compound across the film [32]; these samples exhibit ferromagnetic behavior with the magnetization value increasing with the

thickness of the LMO stack. It is important to emphasize that the change in the magnetic behavior depends on factors such as the size of the system or the quantum confinement, as occurs for the modeled systems in this work.

**4. Conclusions**

Because of the diverse technological possible applications of perovskite thin films, in this work we calculated the electronic DOS and band structure, as well as the atomic magnetic moments, for SFMO, SFO and SMO thin slabs, with a thickness smaller than the corresponding to equivalent films for which experimental data were reported. While SFO and SMO slabs are metallic, the SFMO slab is half-metallic as it is the bulk material; the three systems exhibit a ferromagnetic behavior, which seems to be reinforced by diminishing the Fe content. Perhaps the most remarkable difference between our results and the experimental reports is the bigger cell parameter values that could be associated to the thinnest of our models.

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