Electronic Structure of the Double Perovskite Ba$_2$Er(Nb,Sb)O$_6$

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Abstract. In this work, we present a detailed study of the structural and the electronic structure of the double perovskite Ba$_2$Er(Nb,Sb)O$_6$. All calculations were performed with the Full-Potential Linear Augmented Plane Wave method (FP-LAPW) based on the Density Functional Theory (DFT). From the minimization of energy as a function of volume using the Murnaghan's state equation has been obtained the equilibrium lattice parameter and the bulk modulus of these compounds. The study of the electronic structure was based in the analysis of the electronic density of states (DOS), and the density of charge, showing that these compounds have a total magnetic moment of 3.0 μ_B per formula unit due to Er atoms.

1. Introduction

Currently the complex perovskites with generic formula A$_2$MM'O$_6$ [1-3] have been subject of enhanced scientific studies because the wide range of applications that these materials present on an industrial scale, double perovskites belonging to the series Ba$_2$LnB'O$_6$ (Ln=lanthanide and Y^{3+} and B'=Nb^{5+}, Ta^{5+}, Sb^{5+}) are of interest due to their potential use as substrates for high-Tc superconductors [4,5] and their likely high chemical compatibility with the structurally analogous, oxygen deficient double perovskites, Ba$_2$LnSnO$_{6-\delta}$; a series of interest for use as solid state electrolytes due to their high ionic conductivity [6,7]. Substitution of Nb^{5+}, Ta^{5+} or Sb^{5+} could provide a method of controlling the oxygen stoichiometry of these compounds, potentially minimizing the problems caused by reduction of Ba$_2$LnSnO$_{6-\delta}$ that is thought to be a consequence of the large level of oxygen vacancies in these compounds [6]. Phase transitions in perovskites have long been of interest to solid-state chemists [8]. Previous studies [9, 10], using laboratory X-ray and medium resolution neutron diffraction, reported that the structures in the series Ba$_2$LnSbO$_6$ change from R-3 rhombohedral (tilt system a$^-$a$^-$a$^-$) to Fm-3m cubic (a^{0}a^{0}a^0) symmetry with decreasing size of the Ln^{3+} cation. Conversely the niobate series Ba$_2$LnNbO$_6$ exhibits the sequence: I2/m monoclinic (a$^-$a$^-$c^0), I4/m tetragonal (a^{0}a^{0}c$^-$) to Fm-3m cubic symmetry. That the symmetry increase as the ionic radius of the lanthanide decreases, this is consistent with the increase of the tolerance factor *t*. An increase in the tolerance factor indicates that the volume of the BO$_6$ octahedron is better matched to the size of the AO$_{12}$ polyhedron reducing the need for the octahedral tilting to accommodate this A-site cation. Since octahedral tilting is

responsible for the lowering of the symmetry from cubic, the symmetry tends to increase as the B-type cation gets smaller.

The aim of this work is to carry out a detailed *ab initio* theoretical study of the complex perovskites Ba_2ErSbO_6 and Ba_2ErNbO_6, which were experimentally reported as cubic structures with spacial group Fm3m [11-13]. Our calculations shown that these compounds have a total magnetic moment of 3.0 μ_B per formula unit due to Er atoms

2. Computational Details

The calculations were performed using Full Potential Linearized Augmented Plane Wave (FP-LAPW) method, within the Density Functional Theory formalism [14], Wien2k code [15]. The exchange-correlation potential was described using the Perdew–Burke–Ernzerhof [16] expression, based in the Local Spin Density Approximation (LSDA) and Generalized Gradient Approximation (GGA) [17]. In all calculations, we used the next muffin-tin radius $R_{MT}(Ba)=2.5$, $R_{MT}(Er)=2.3$, $R_{MT}(Nb, Sb)=2.05$ and $R_{MT}(O)=1.60$ bohr; and the parameter $R_{MT} \times K_{max}$ was kept equal to 7 and $G_{max} = 12$. The irreducible Brilloiun zone was described with 286 k-points, a mesh of 21×21×21. Furthermore, in all calculations we have considered spin polarization and the parameter of convergence was the variation of charge 10^{-5} a.u., the core and valence states are treated in the fully and scalar relativistic scheme, respectively.

In the present work, we have considered these compounds with cubic crystalline structure Fm-3m (225), see Figure 1.
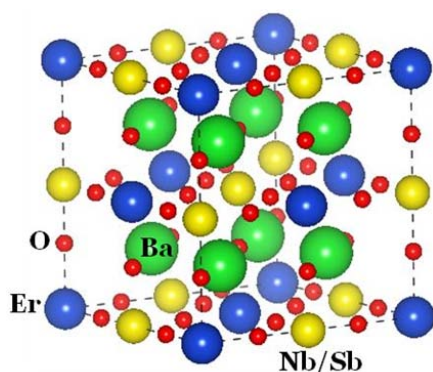

Figure 1: Cubic crystal structure Fm-3m of the compound $Ba_2(Nb,Sb)ErO_6$.

3. Results and discussion

In order to obtain the equilibrium structure, the total energy vs. lattice parameter curves were obtained for BaEr(Nb,Sb)O compounds using LSDA and GGA. These curves were fitted using the Birch-Murnaghan's state equation [18] to determine the equilibrium lattice parameters (*a*), bulk modulus (B) and their derivate (B'). In Table 1 we shows these values together experimental data obtained from the bibliography [11-13]. For both compounds the ground state belong to GGA calculations, where the *a* value for these compounds are in agree with experimental one.

Table 1: Theoretical value of a (Å), B (GPa) and B' of the compound $Ba_2Er(Nb,Sb)O_6$.

		a (Å)	B (GPa)	B'
Ba_2ErNbO_6	LDA	8.3176	161.3	5.1
	GGA	8.4956	131.2	5.6
	Exp.	8.4270[11]		
		8.4193[12]		
Ba_2ErSbO_6	LDA	8.3124	146.7	3.9
	GGA	8.5048	123.8	5.9
	Exp.	8.3960[12]		
		8.3904[13]		
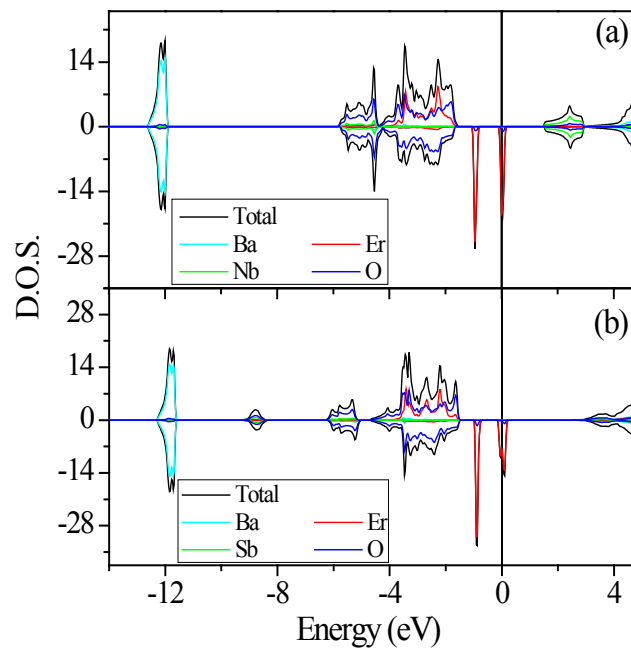
Figure 2: Total density of states and projected per atom of the compound
(a) Ba_2ErNbO_6 and (b) Ba_2ErSbO_6.

In figure 2, we show the total density of states (D.O.S.) of these compounds where and by atom. In both compounds the DOS belong to Ba atoms are locate in depth energies values without any hybridization with other atomic orbitals. Between -6.0 and -4.0 eV there are hybridization between the $4d$-(Nb, Sb) and the $2p$-O orbitals whereas between -4.0 and -1.5 eV we found hybridization of the $2p$-O and $4f$-Er orbital, but only in the majority DOS. Only in the Ba_2ErSbO_6 compound is possible see a hybridization $5s$-Sb and $2s$-O orbitals. In both compounds, the DOS of the Er atom show a dislocation and different population between the majority and minority DOS, producing a magnetic moment in this atom close to 2.86 μ_B. In the figure 3, we show the difference of the density of charge up and down in the plane (100) for both compounds, where is possible to see a mayor concentration of this difference around to the Er atoms, showing the magnetic character of these atoms. This is the reason why these compounds have a magnetic ground state with a magnetization of 3.0 μ_B per formula unit, agreeing with experimental studies for the case of the Ba_2ErSbO_6 [13].
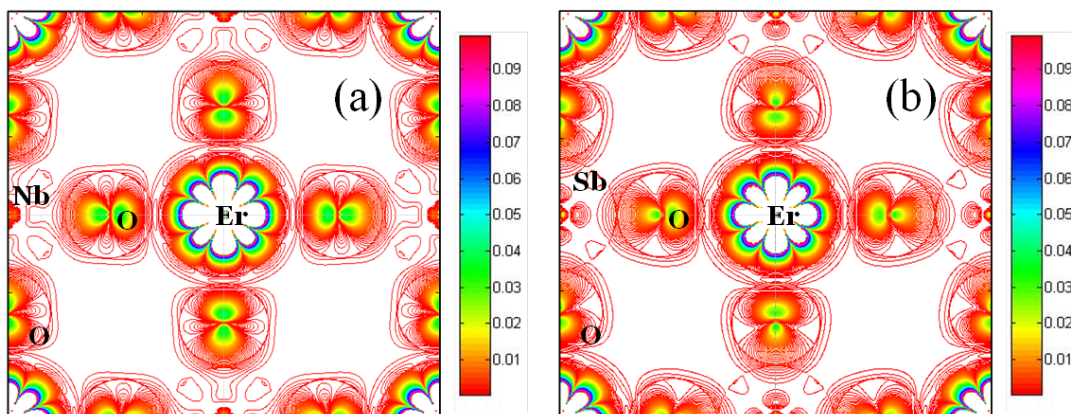
Figure 3: Difference between the charge density up and down in the plane (100)
of the (a) Ba_2ErNbO_6 and (b) Ba_2ErSbO_6.

4. Conclusions

The structural and electronic properties of the $Ba_2Er(Nb,Sb)O_6$ perovskite compound in the cubic structures were calculated using the method of Linearized Augmented Plane Wave on the Generalized Gradient (GGA) and Local Density (LDA) approximations with similar results. By minimizing the energy as a function of volume, structural characteristics such as the total energy, the equilibrium volume, the volume module, and the lattice parameters that minimize energy of the system were determined, where the equilibrium lattice parameter is in agree with experimental data. Furthermore, from analysis of the DOS and the density of charge, was possible explain the magnetic ground state of these compound, with a magnetization of 3.0 μ_B per formula unit due mainly to the contribution of Er atom.

Acknowledgments

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