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Structural, electronic and magnetic properties of FCC Ba_2CoBO_6 [B = Mo, W, Re, Os]: LSDA+*U*+SOC comparative investigation

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ABSTRACT

First-principles calculations by the full potential linear muffin-tin orbital (FP-LMTO) method using local spin density approximation (LSDA), taking into account of both spin orbital coupling (SOC) and strong correlation (*U*) within the framework of spin-polarized density functional theory (DFT), were carried out for the structural, electronic and magnetic properties of a series of double perovskites Ba_2CoBO_6 (B = Mo, W, Re, Os). Structural optimizations of lattice constants show that all Ba_2CoBO_6 compounds crystallize in face-centered cubic (FCC) system with space group of ($Fm\bar{3}m$), in good agreement with the experimental values. The relative stability of ferromagnetic (FM) and antiferromagnetic (AFM) orders is discussed. It is shown that it consistent with experimental results and AFM order is obtained when using LSDA and LSDA+*U* methods. The magnetic results show that the double perovskites Ba_2CoBO_6 are AFM through the anti-coupling Co^{2+} $(3d^7)\uparrow$–O^{2-} (2p)–B^{6+} $(4d/5d)^n\downarrow$, where $n = 0$, 1 or 2. DFT results show that the Ba_2CoBO_6 are half-metallic (HM) with energy-gaps in spin-up bands, but if B = Mo, it shows metallic nature in LSDA results, and it established that the *U* responsible for the AFM-HM in Ba_2CoBO_6.

1. Introduction

Experimental and theoretical research investigations on magnetic materials have been increasing over the past half-century, mainly due to their unique and interesting structural, electronic, magnetic and optical properties. Transition-metal double perovskites class belong to the large family of crystalline magnetic materials. Double perovskite materials have attracted special attention in many applied and fundamental area of solid-state physics and advanced materials science due to exotic electronic, magnetic and optical properties. Various properties were observed in this class, for example, colossal magnetoresistance (CMR) in Sr_2MMoO_6 (M = Cr, Fe) [1–4], tunnel magnetoresistance (TMR) in Sr_2FeMoO_6 [5], half-metallicity (HM) in Ca_2FeReO_6 and Ba_2FeMoO_6 [6], magnetoelectricity in Sr_2CoMoO_6 [7]. Double perovskites with the general chemical formula of A_2MBO_6 result from the ordering of M and B on the octahedral site of primitive perovskite AMO_3 in the rock-salt arrangement. Varying different cations with other alkaline ions at A-site or transition-metals at M–B sites very rich structural, electronic, magnetic and optical properties can be obtained. However, the understanding of the relation between structural, electronic, magnetic and optical properties is a hot field of research studies. Magnetic double perovskites A_2MBO_6 with (B = Re) were first proposed by Longo and Ward in the 1960s [8]. According to those authors, A-site is an alkaline earth-metal and M–B sites were occupied by magnetic and non-magnetic transition-metals, respectively. Later in 1998s, the HM electronic nature of the well-known double perovskite Sr_2FeMoO_6 was established by Kobayashi et al. [1]. HM behavior can be characterized by the difference between the conduction electrons. The density of states (DOS) as function of energy clearly evidence that the spin-up bands (DOS↑) show energy-gap (E_g) at the Fermi level (E_F), while the spin-down bands (DOS↓) overlap and cross the E_F, due to the strong Fe (3d)–O (2p)–Mo (3d) hybridization. The HM-AFM property has been observed in many double perovskite compounds, such as Sr_2OsMoO_6 presents 100% spin polarization of conduction electrons crossing the E_F [9,10]. Extensive research on double perovskites are related to the probable technological applications in spintronics field, such as spin valves, sources for spin polarized electrons and magnetic information storage devices.

Barium double perovskites Ba_2MBO_6 have revealed a variety of crystal structures and electronic and magnetic properties. Antiferromagnetic Ba_2MBO_6 with M = magnetic ion and B = non-magnetic ion characterized by the super-exchange interaction between the magnetic ions via an array of non-magnetic ions. When Ba_2MBO_6 include transition-metal ions within M or B sub-lattice, the magnetic properties are strongly influenced by the ordering of the

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cations within this sub-lattice. Like other known double perovskites, Ba_2CoBO_6 not found enough attention, however, there are few experimental studies focused on Co-based double perovskites Ba_2CoBO_6. Martínez-Lope et al. analyzed and reported that Ba_2CoMoO_6 and Ba_2CoWO_6 were antiferromagnetic materials with low Néel temperatures of ($T_N = 27$ K) and ($T_N = 19$ K), respectively [11]. Hirama et al. investigated the La-substitution effects on the antiferromagnetic insulator Ba_2CoMoO_6 [12]. Recently, Zhang et al. explored Ba_2CoMoO_6 as anode material for solid oxide fuel cells [13]. Also, López et al. reported that A_2CoWO_6 crystallized in a cubic structure with antiferromagnetic when A = Ba [14]. Earlier, Sleight and Weiher reported that Ba_2CoReO_6 was antiferromagnetic with ($T_N = 41$ K) [15].

In this paper, the structural, electronic and magnetic properties of double perovskites Ba_2CoBO_6 (B = Mo, W, Re, Os) have been investigated. The crystal structure information, ground states, band-gaps, and total and partial densities of states are calculated for the first time by using the first-principles of the full potential linear muffin-tin orbital (FP-LMTO) method within the Von Barth-Hedin localized spin density approximation (LSDA). It is expected that the present study will help in understanding how the B-site substitution and correlation energy U affect the structural, electronic and magnetic properties of Ba_2CoBO_6. In addition, the paper will also cover the lack theoretical data on physical properties of Co-based double perovskites Ba_2CoMoO_6, Ba_2CoWO_6, Ba_2CoReO_6 and Ba_2CoOsO_6.

2. Computational method

First-principles density functional theory (DFT) calculations within localized spin density approximation (LSDA) [16,17] for the exchange–correlation functional have been used to study the structural, electronic and magnetic properties of double perovskites Ba_2CoBO_6 (B = Mo, W, Re, Os). The computational method was considered the full potential linear muffin-tin orbital (FP-LMTO) [18] implemented in the fast and efficient LMTART software package [19,20]. FP-LMTO method, for which the self-consistent (SCF) version is yet to be available, relies on the SCF potential borrowed from the LMTO calculations. For SCF calculation with plane-wave (PLW) basis, the number of k points was chosen to be 120 and has checked for convergence. The commonly used criterion relating the PLW and angular momentum cutoff ($L_{Max} = R_{Max} \times K_{Max}$) was taken to be 6.0, where R_{Max} and K_{Max} are the maximum muffin-tin (MT) sphere radius and the PLW cutoff for the basis, respectively. In this study, the atomic MT sphere radii were chosen from the charge neutrality condition inside the spheres; so that the total unit cell volumes were close to the experimental ones, see Table 1. Spin orbital coupling (SOC) has been included in the calculations. For the SCF–LMTO calculations within the atomic PLW approximation, no empty spheres were introduced since the structures are closed-packed. The self-consistency was achieved with ($8 \times 8 \times 8$) k-points in the Brillouin zone. Furthermore, the calculations have been carried out within the LSDA+U in PLW basis to take into account the missing correlation effect beyond the LSDA [16,17]. In LSDA+U calculations, the near-maximum values of Coulomb U and exchange J correlation parameters were selected from the reasonable ranges reported in the literature for double perovskites; for Co (3d) is $U = 3.0$ eV–6.0 eV and for B (4d/5d) is $U = 1.0$ eV–2.0 eV [21–23]. Here, U (Co) = 5.0 eV and U (B) = 1.0 eV, and J (3d, 4d, 5d) = 0.89 eV are used.

Table 1
Size of atomic radii of the MTSs (in atomic unit) used in the FP-LMTO calculations.

Compound	Ba^{2+}	Co^{2+}	B^{6+}	O^{2-}
Ba_2CoMoO_6	3.578	1.987	2.139	1.592
Ba_2CoWO_6	3.831	2.530	2.147	1.492
Ba_2CoReO_6	3.546	2.018	2.082	1.560
Ba_2CoOsO_6	3.531	2.003	2.067	1.575

3. Results and discussion

3.1. Structural properties of Ba_2CoBO_6

Ba_2CoBO_6 (B = Mo, W, Re, Os) double perovskites crystallize in face-centered cubic (FCC) with space-group of ($Fm\bar{3}m$; No. 225). The lattice constants are approximately equal to ($a \approx 8.0$ Å). Table 2 displays the ionic radii of B ions, tolerance factors, formula unit volumes, lattice constants (a,b,c), oxygen positions in O (x,0,0) and the average bond-lengths of ⟨Co–O⟩ and ⟨B–O⟩. The lattice constants are around the ideal value ($a = 2a_0$; $a_0 = 4$ Å) and depend mainly on the ionic radii in Ba_2CoBO_6; Ba^{2+} ($r = 1.61$ Å), Co^{2+} ($r = 0.65$ Å, in high-spin, and $r = 0.545$ Å in low-spin), B^{6+}, see Table 2, and O^{2-} ($r = 1.41$ Å). As shown in Table 2, the oxygen position x varies in small amount ($\Delta x = \pm 0.1$) and depends on the B-site. The calculated crystallographic structural data of Ba_2CoBO_6 were compared with the available previous experimental data. Unfortunately, Ba_2CoOsO_6 has not been studied yet, and no experimental data are available in the database. However, the structural data can be estimated from the parent compound Sr_2CoOsO_6 [22]. The common atomic sites and positions (x,y,z), and valence states in the FCC crystal structure of formula units of Ba_2CoBO_6 are Ba^{2+} at 8c (0.25,0.25,0.25), Co^{2+} at 4a (0,0,0), B^{6+} at 4b (0.5,0.5,0.5) and O^{2-} at 24e (x,0,0). The structural results obtained in this study are in close agreement with those obtained experimentally [11,14,23,24], see Fig. 2. It can be seen that there is linear increase of lattice constant and formula unit volume if B = Mo, W, Re and Os in Ba_2CoBO_6.

As seen in Fig. 1, from Ref. [20], the 3D geometric crystal structure of the cubic formula unit of double perovskite Ba_2CoBO_6 in $Fm\bar{3}m$ symmetry can be described by the FCC arrangement of Co and B ions in rock-salt order. In this crystal structure, both Co^{2+} (0,0,0) and B^{6+} (0.5,0.5,0.5) ions form FCC lattice with the displacement of half of the lattice constant. The oxygen ions O^{2-} (x, 0,0) locate near the center of each nearest-neighboring Co–B pair and the bond-length of $\langle Co^{2+}–O^{2-} \rangle$ and $\langle B^{6+}–O^{2-} \rangle$ is approximately equal to 2.0 Å, Table 2. Only six O^{2-} ions around the center of Co^{2+} and B^{6+} ions formulate the CoO_6 and BO_6 octahedra in a tilt system of ($a^0a^0a^0$), whereas the Ba^{2+} ions are located in the cavities between CoO_6 and BO_6 octahedra. Moreover, to verify whether the crystal structure of double perovskite is distorted from the ideal structure the tolerance factor (t) is used to evaluate the symmetry deviations, it is defined as: $t = (r_{Ba} + r_O)/\sqrt{2}((r_{Co} + r_B)/2 + r_O)$. Where r_{Ba}, r_{Co}, r_B, r_O are the radii of the different cations and oxygen in Ba_2CoBO_6. This factor describes the stability of the double perovskite structure; ($t = 1.0$) represents the ideal cubic structure. The crystal structure of Ba_2CoBO_6 is stable and adopt cubic symmetry ($Fm\bar{3}m$) with tolerance factors closed to 1.0, see Table 2. Accordingly, the CoO_6 and BO_6 octahedra did not deviate from the cubic crystal structure (Tilt = 0.0) in order to fill the space, see Fig. 1.

Double perovskites Ba_2CoBO_6 adopt the Na^+Cl^- arrangement, and can be viewed as a network of regular arrangement of corner-sharing CoO_6 and BO_6 octahedra, with Ba-cations occupying the voids formed by these octahedral. CoO_6 and BO_6 alternate along the three crystallographic directions (a,b,c). As known, Ba^{2+}-cations has a large size ($R^{2+}_{Ba} = 1.61$ Å), so, the octahedral network is not tilted (Tilt = 0.0^0), keeping ⟨Co–O–B⟩ angle at 180°. In addition, there is a perfect 1:1 B-site ordering of Co and B, due to the large difference in size and charge existing between Co^{2+} and