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First Principles Investigation of Electronic, Structural, Magnetic and Thermodynamic Properties of KXO_3 (X=Sr and Ba) Perovskite

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Abstract

The structural, electronic, magnetic and thermodynamic properties of two novel perovskite compounds KXO_3 (X=Sr and Ba) have been investigated from First Principles calculation. Results from the electronic properties of the two compounds reveal that they are half-metals. Their formation energy also show that these compounds can be synthesized experimentally. Their magnetic property reveals that the compounds are more stable in the ferromagnetic states with magnetic moment of $3\mu_B$ each for the two compounds. The two perovskites are found to be thermodynamically stable and having specific heat capacities of 123.18 J/Kmol (124.90 J/Kmol) for $KSrO_3$ ($KBaO_3$).

1. Introduction

Half metals have gained the interest of researchers over the years due to their unique properties which find application in spintronics industry [1]. They are known to behave as a metal in one spin orientation and as a semiconductor in another spin orientation [2]. They are also known to possess 100% spin polarization around the Fermi energy. Half metal was first predicted in half Heusler alloy MnNiSb in 1983[3] and ever since several compounds such as the Heusler alloy family [4-6], perovskites [2], double perovskites [7], oxide of transition metals [8] have been found to possess half-metallic property either theoretically or experimentally. Among these compounds that have been found to possess the half-metallic property, perovskite is a special type of compound that exhibit vast unique properties [2] which makes it find application in technological industries such as spintronics and optoelectronic industries. Perovskites are known to have the general form ABO_3 and crystallize in cubic structure (Pm-3m, no. 221), orthorhombic structure (Pnma, no. 62) and tetragonal structure (I4/mcm, no. 140). The cubic structure is commonly studied from first principles calculation. Most of the half-metallic perovskites studied have transition elements in them [9,10] and it is the transition elements that contribute the highest local magnetic moment. Recently, some researchers have studied perovskites without transition element [2,11] and it is observed that the oxygen atoms are responsible for the magnetic moments of such compounds. This is due to the fact that oxygen is highly electronegative thereby accepting electrons from the two other elements A and B making the oxygen atom have high electron spin density. More perovskites without transition elements are yet to be explored and when more are explored this will give room for experimentalist to make choice among verities when designing half-metals for spintronics purpose. In this work, we focus on a novel perovskites compounds without transition elements KXO_3 (X=Sr and Ba). Structural, electronic, magnetic and thermodynamic properties of these compounds have been investigated from first principles

calculation and the results are discussed in the results. The remaining part of the work is organized as follow: Section 2 shows the methodology, Section 3 presents the results and discussion and finally we conclude with conclusion in Section 4.

2. Methodology

The first principles calculation was carried out using the projected augmented wave (PAW) with the plane-wave pseudopotential within the generalized gradient approximation as implemented in the quantum espresso (QE) code [12]. A variable cell relaxation was carried out in order to achieve structural optimization. The total ground state energy was achieved using a kinetic energy cut-off of 75Ry and 65Ry for $KBaO_3$ and $KSrO_3$ respectively, while the K-point used are 11X11X11 (10X10X10) for $KBaO_3$ ($KSrO_3$). In order to get the optimized lattice constant for both the ferromagnetic states and the nonmagnetic states for the two compounds, we plotted the graph of the total energy vs the lattice constants an fitted to the Murnaghan equation of states. The results are presented in Table 1. Thermodynamic properties were computed with the help of thermo_pw code [13].

3. Results and Discussion

3.1 Structural properties

Table 1 presents the structural parameters computed in this work. The perovskite is known to crystallize in the simple cubic type of the $CaTiO_3$ structure with space group Pm-3m (no. 221) and trukturbericht Designation $E2_1$. The crystal structure of KXO_3 (X=Ba and Sr) is shown in Figure 1. The lattice constant, the bulk modulus as well as the pressure derivative describing the structural properties of the two perovskites compounds are presented in Table 1. Figures 2 and 3 will be discussed in details under the magnetic property in Section 3.3. It is observed that the lattice constant of $KSrO_3$ in the ferromagnetic state is lesser than that of $KBaO_3$ also in the ferromagnetic state. This is due to the fact that Sr has smaller atomic mass when compared with Ba. KXO_3 is found to be stiffer than $KBaO_3$ from the bulk modulus results. We computed the formation energies of KXO_3 (X=Ba and Sr) in order to ascertain if they can be synthesized experimentally. If the formation energy is negative, it implies that the compounds can be synthesized in the lab and will remain stable. The formula used in computing the formation energies is given in Equ.1[14].

$$E_f(KXO_3) = E(KXO_3) - (E(K)+E(X)+3/2E(O_2)) \quad (1)$$

where $E(KXO_3)$ is the total energy of the compound, E(K) is the total energy of potassium per number of atoms per unit cell, E(X) is the total energy of barium and strontium per number of atoms per unit cell and $E(O_2)$ is the total energy of oxygen per number of atoms per unit cell. The formation energy of the two perovskites are presented in Table 1. The results indicate that KXO_3 (X=Ba and Sr) can be synthesized experimentally

Table 1: Lattice parameter a, bulk modulus (B), pressure derivative (B') the magnetic moment (M) and formation energy (E_f) of KXO_3.

Compounds	Method	a(Å)	B(GPa)	B'	M(μ_B)	E_f(eV)
$KSrO_3$	FM	4.819	26.3	3.61	3	-5.671
	NM	4.725	22.6	5.48		
$KBaO_3$	FM	4.978	22.8	6.43	3	-5.283

NM	4.662	32.5	5.39

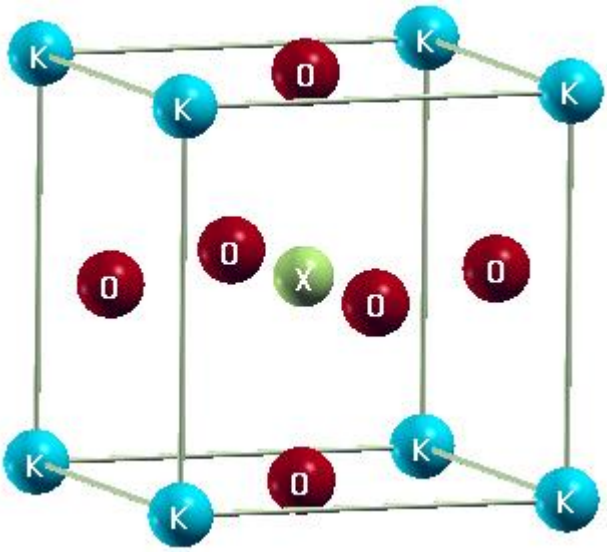

Figure 1: Crystal structure of KXO_3 (X=Ba and Sr)

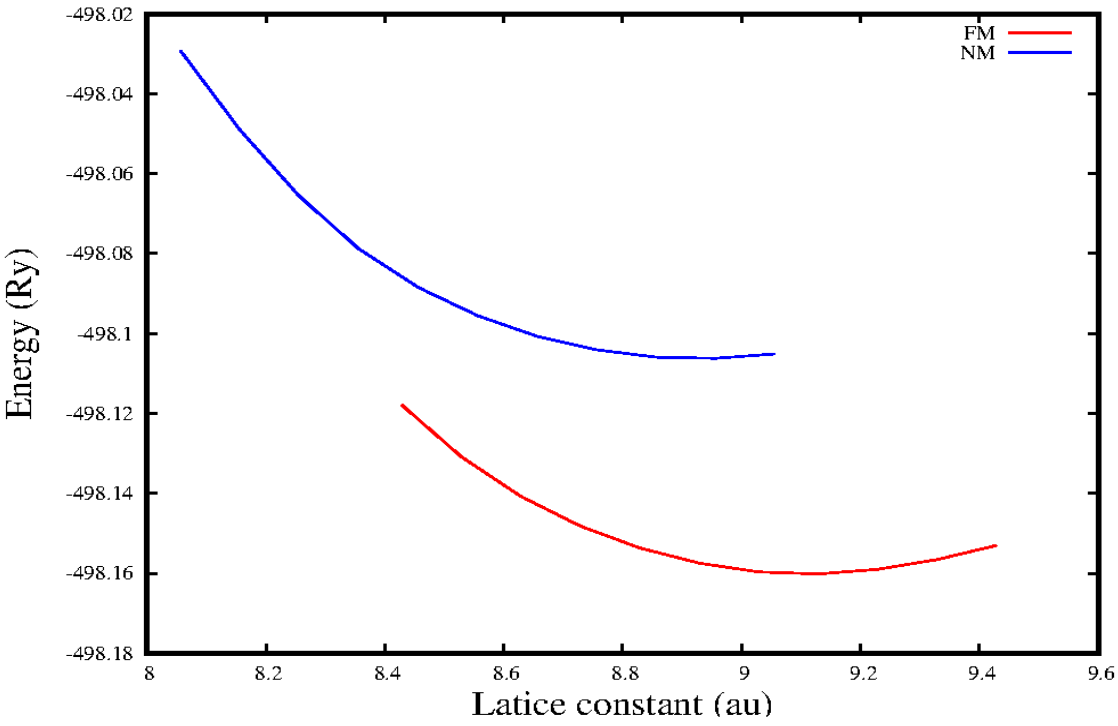

Figure 2: Total energy versus lattice constant of $KSrO_3$

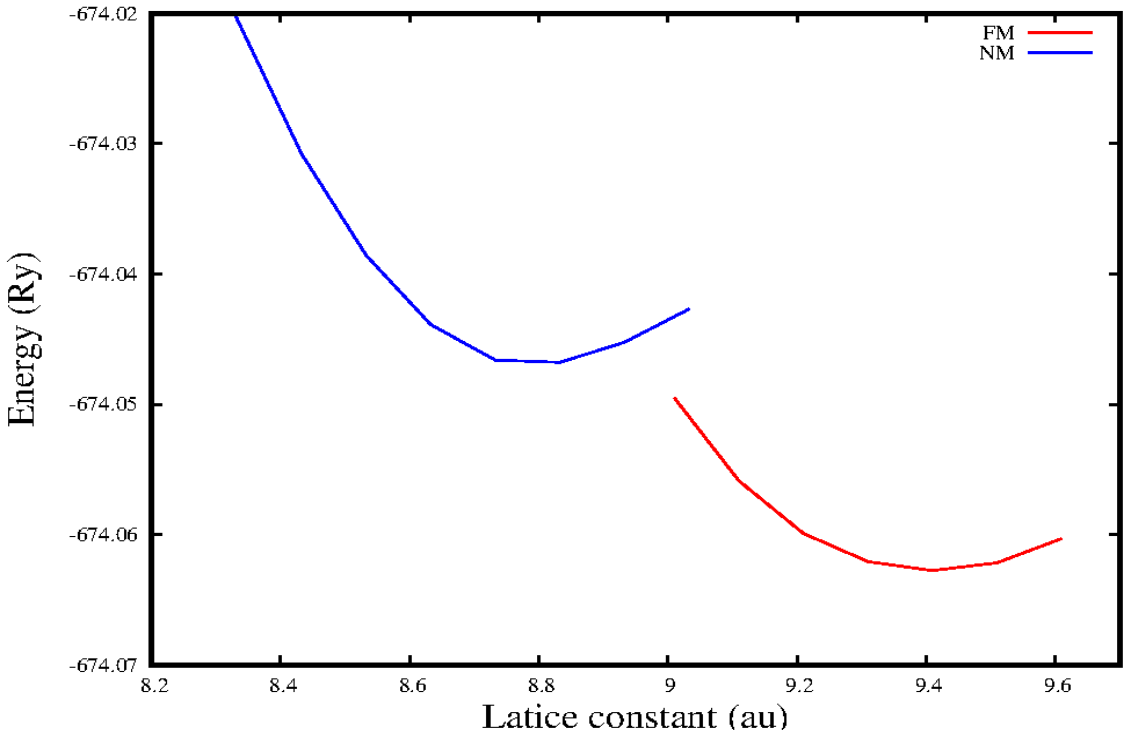

Figure 3: Total energy versus lattice constant of $KBaO_3$

3.2 Electronic properties

The electronic properties of KXO_3(X=Sr and Ba) are presented in Figures 4 and 5 with each diagram having the band structure and partial density of state (PDOS) in the majority spin channel and the minority spin channel. It is observed that the band structures of KXO_3(X=Sr and Ba) for the majority spin channels indicate semiconducting behavior with direct band gaps of 5.07eV and 4.5eV for $KSrO_3$ and $KBaO_3$ respectively. While the band structure of both compounds in the minority spin channel indicates a metallic behavior. This unique property indicates that the two compounds are half-metals. The middle graphs in Figures 4 and 5 represent the PDOS which reveal the contribution of each atomic orbitals.

The half metallic gap (HM_{gap})is another important parameter in the study of half-metals. It is used to describe the half-metallic character of half metals. It is said to be the difference between the highest value of the valence band and the Fermi level [15]. It is expressed as [16].

$$HM_{gap} = min(|E_F - E_{VMB}|, |E_F - E_{CMB}|) \quad (2)$$

The half-metallic gap computed for both compounds are 0.854eV(0.524eV) $KSrO_3$ ($KBaO_3$). This half-metallic gap is also known as the spin-flip gap and it is the minimum energy required to flip a majority-spin electron from the valence band maximum to the minority spin Fermi level [17]. From the spin-flip gap of both compounds, $KBaO_3$ has the lower energy needed to flip majority-spin electron from the valence band maximum to the minority spin Fermi level. Since the two compounds have similar structures, their DOS have similar pattern with the p-orbitals of the oxygen contributing more around the Fermi energy. The gap splitting is between the p-orbitals of oxygen atom and the s orbitals of the potassium atom. The contribution of the other orbitals are very weak as seen around the Fermi energy.

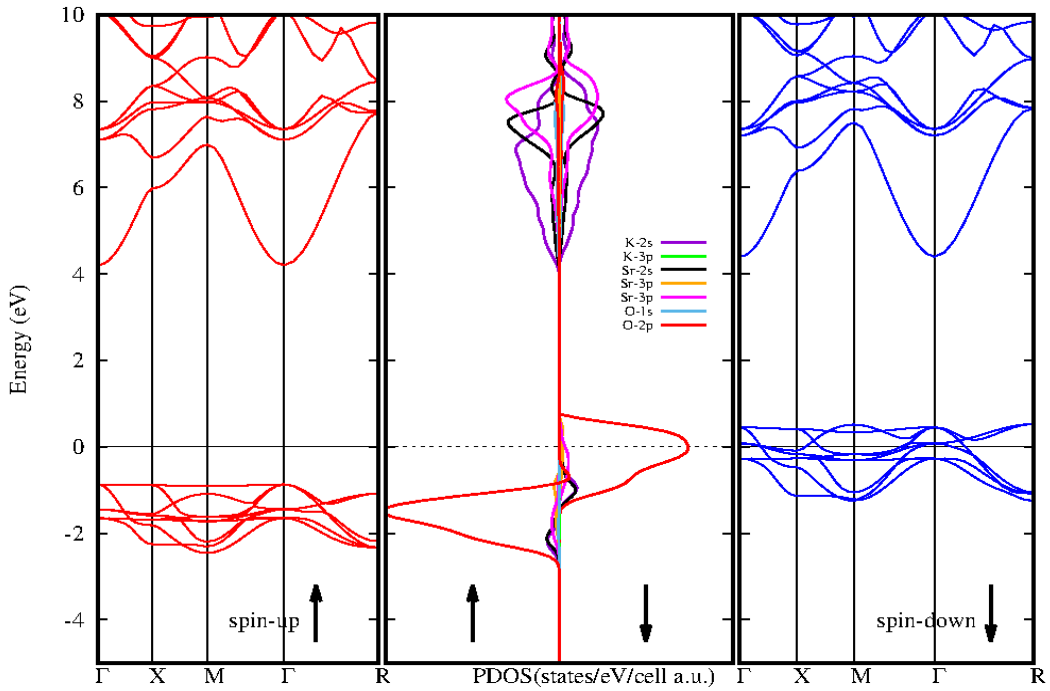

Figure 4: Electronic band structure and partial density of state of $KSrO_3$

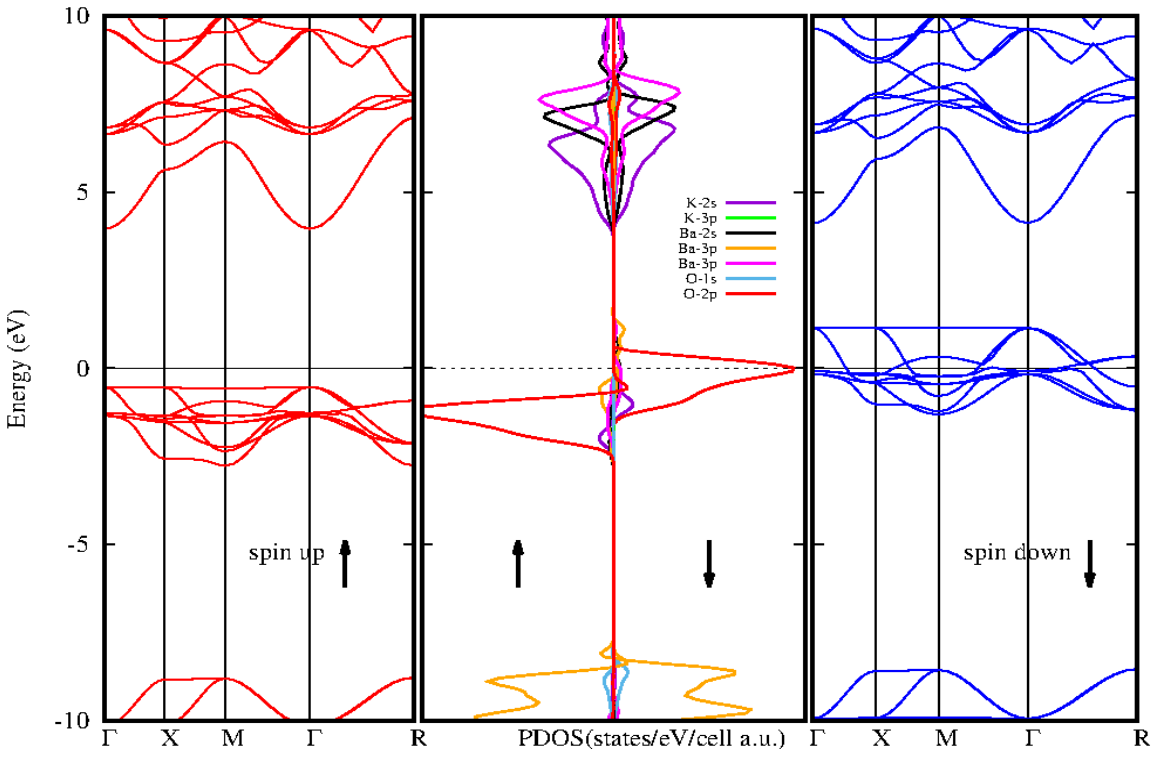

Figure 5: Electronic band structure and partial density of state of $KBaO_3$

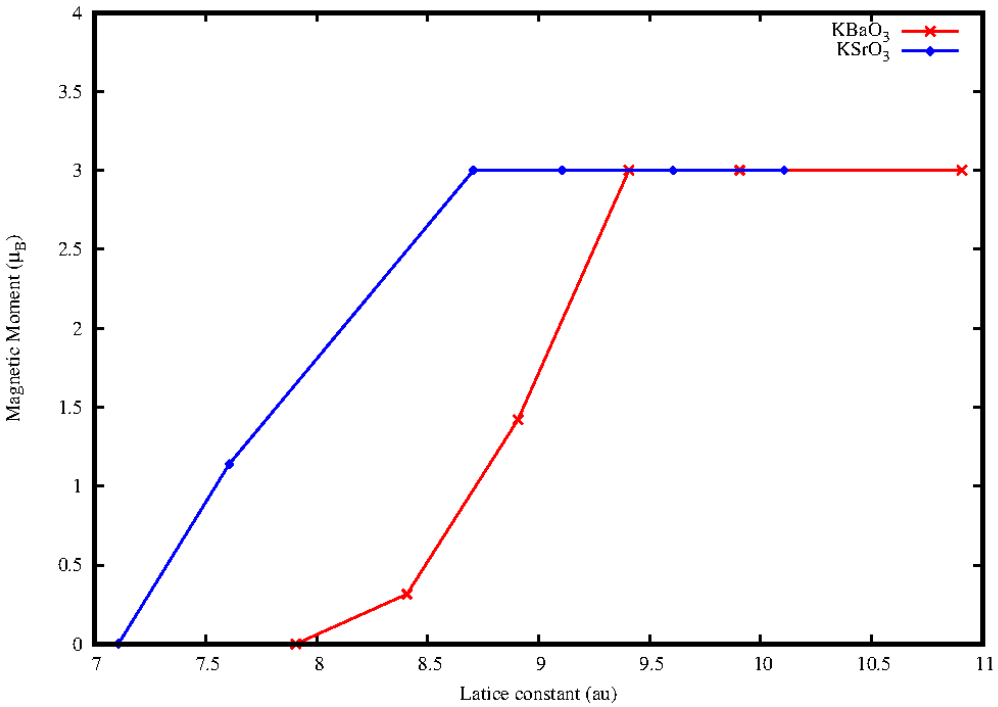

Figure 6: Magnetic moment versus lattice constant of KXO_3 (X=Sr and Ba)

3.3 Magnetic Properties

The magnetic properties of KXO_3(X=Sr and Ba) have been investigated and their results are shown in Table 1 and Figures 2 and 3. From Figures. 2 and 3 it is evident that the two perovskites are ferromagnetic (FM) in nature having the lowest total energies when compared with the non-magnetic (NM) states. We further computed the magnetic moments of KXO_3(X=Sr and Ba) and both are found to have values of $3\mu_B$. Atoms of K, Ba and three atoms of O contribute local magnetic moment of $-0.0207\mu_B$, $0.1148\mu_B$ and $0.9901\mu_B$ to the compound $KBaO_3$. Also, Atoms of K, Sr and three atoms of O contribute local magnetic moment of $-0.0232\mu_B$, $0.0307\mu_B$ and $1.0379\mu_B$ to the compound $KSrO_3$. Most materials loose their half-metallic properties when they are subjected to strain, this is due to the fact that their magnetic moments vanish as the compounds undergo strain. Figure 6 shows the behavior of the magnetic moment under strain for both compounds. It is observed that the magnetic moment vanishes at a strain of about 7.9a.u for $KBaO_3$ and about 7.1a.u for $KSrO_3$.

3.4 Thermodynamic Properties

The results of the thermodynamic properties of KXO_3(X=Sr and Ba) are presented in Table 3 and in Figure 7. The specific heat capacities at constant volume of both perovskites as shown in Table 3 are close due to the fact that they have similar element that constitute them. The zero-point energy of $KSrO_3$ is higher than that of $KBaO_3$. This zero point-energy is the energy of a material at absolute zero temperature. The Debye temperature gives information about the thermal conductivity of a material, the higher the value the higher the thermal conductivity. $KSrO_3$ has higher Debye temperature compared to $KBaO_3$.

Table 3: The calculated specific heat capacity C_v(J/Kmol) at 300K, Debye temperature θ_D(K) and the zero-point energy E_o(kJ/Nmol), for the two compounds.

Compounds	C_v	θ_D	E_o
$KSrO_3$	123.18	161.16	7.54
$KBaO_3$	124.90	30.17	1.41

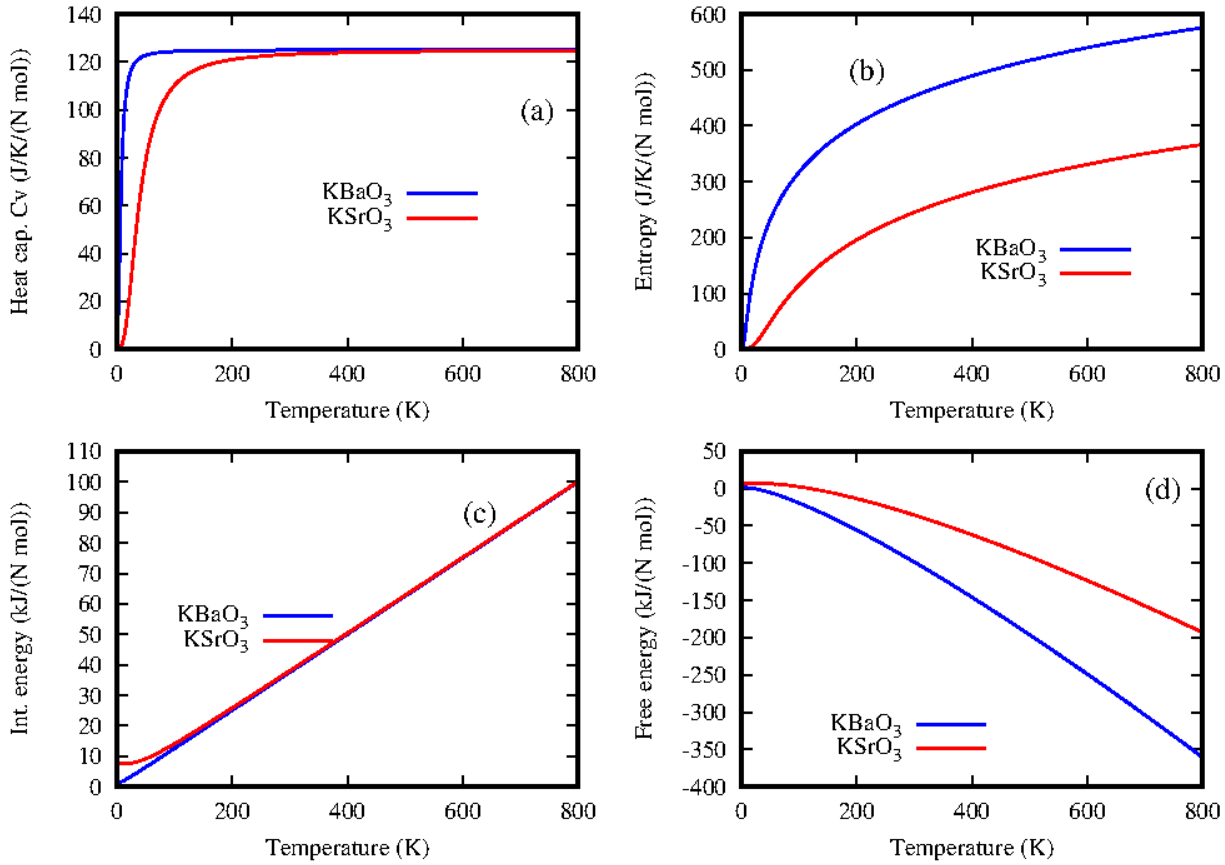

Figure 7: The calculated (a) Specific heat capacity, (b) the entropy, (c) Internal energy and (d) the Gibb's free energy for KXO_3(X=Sr and Ba).

4. Conclusion

The structural, electronic, magnetic and thermodynamic properties of two novel perovskite compounds KXO_3 (X=Sr and Ba) have been investigated from first-principles calculation in this paper. These compounds are found to be ferromagnet and half-metals in their cubic structure. They can also be sythesized experimentally especially from their negative values of formation energies. Their bulk modulus show that the compounds are structurally stable and soft. They are observed to be thermodynamically stable with high specific heat capacities.

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