Materials Chemistry and Physics xxx (2015) 1–8

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba)

Zahid Ali [a, *], Imad Khan [a], Iftikhar Ahmad [a], M. Salman Khan [a], S. Jalali Asadabadi [b]

[a] Center for Computational Materials Science, University of Malakand, Chakdara, Dir (Lower), Pakistan
[b] Department of Physics, Faculty of Science, University of Isfahan, Hezar Gerib Avenue, Isfahan, 81744, Iran

HIGHLIGHTS

- $MTaO_3$ (M = Ca, Sr and Ba) perovskites are investigated theoretically in the frame work of density functional theory.
- Mechanical properties explain the stability of these compounds and show that $BaTaO_3$ is more ductile.
- The magneto-electronic studies reveal the paramagnetic metallic nature of these compounds.
- Significant electrical conductivity is observed above room temperature.

ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form
29 April 2015
Accepted 29 May 2015
Available online xxx

Keywords:
Ceramics
ab initio calculations
Mechanical properties
Electronic structure
Electrical conductivity
Magnetic structures

ABSTRACT

In the present density functional studies, structural, mechanical and magneto-electronic properties of $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ perovskites have been investigated. The calculated structural parameters by DFT and analytical methods are found consistent with the experiments. The analytically calculated tolerance factors of these compounds as well as their mechanical properties show that they are stable in the cubic phase. Furthermore elastic properties show that these materials are ductile in nature and confirm that $BaTaO_3$ is harder than the rest compounds. The calculated spin dependent magneto-electronic properties reveal the paramagnetic metallic nature of these compounds. The electrical conductivity curve demonstrates significant conductivity above room temperature. On the basis of the presented properties it is expected that these compounds could be efficient electrode materials and need experimental investigations.

1. Introduction

To meet the requirements of the advanced technological needs, material scientists are searching for cheap and efficient materials with improved properties. Perovskites have been widely studied because of their potential technological applications in optoelectronics, high capacity memory cells, substrates, catalytic electrodes in fuel cells, high temperature superconductors and in spintronics. The unique physical properties of these compounds like superconductivity at high temperature, colossal magneto-resistivity, giant-magnetoresistivity [1,2], ferroelectricity, piezoelectricity and ionic conductivity make them significant in various advance technological applications [3–5].

Recently paramagnetic perovskites materials with metallic nature have attracted the focus of materials scientist [6], because of their interesting properties such as electrical conductivity, hardness, current load and crystal structure which make them potential candidate for electrode materials. The basic advantage of the metallic electrodes materials is their electrical conductivity and mechanical stability.

All ceramic electrodes have been intensively studied in the last two decades [7]. Several recent review articles have provided excellent overviews of the current ceramic electrode materials development [8–10]. Ceramics offer a number of possible advantages over metals, depending on the composition and preparation methods. The key component towards the realization of functional oxide materials in electronics is a high quality electrode material that is structurally and chemically compatible with perovskites and demonstrates very low electrical resistivity. $SrRuO_3$ has been widely used as a conducting oxide for the electrode materials [11].

* Corresponding author. Department of Physics, University of Malakand, Chakdara, Dir (Lower), Pakistan.
E-mail address: zahidf82@gmail.com (Z. Ali).

http://dx.doi.org/10.1016/j.matchemphys.2015.05.072
0254-0584/

Ta based cubic oxides like $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ are interesting compounds of the perovskite family. The cubic structure of $CaTaO_3$ is reported by Gasperin [12]. In his experimental studies he found that the lattice constant of the compound is 3.88 Å. In experimental studies Rodriguez et al. [13] observed that the space group of the cubic $SrTaO_3$ is Pm-3m (221) whereas its lattice constant is 1% greater than the lattice constant of the $SrTiO_3$. In another studies [14] it has been shown that the sub-layer of $SrTaO_3$ has high formation energy for oxygen vacancy and hence it can block the oxygen migration towards the electrodes. Different physical properties of Mg doped $BaTaO_3$ are studied by Wakino [15]. He found that $Ba(Mg_{1/3},Ta_{2/3})O_3$ possess the highest frequency for moderate dielectric constant and is used as dielectric resonators, oscillators and filters for the radio frequency range. But the existence and physical properties of pure $BaTaO_3$ is yet to be reported. In this particular study we investigate theoretically the structural and other physical properties of $BaTaO_3$ for the first time.

In this work structural, mechanical, electronic and magnetic properties of the cubic perovskites $MTaO_3$ (M = Ca, Sr and Ba) are investigated. To explore magneto-electronic behavior of these compounds for their possible applications in these first ever calculations of this nature, we used the full potential linearized augmented plane waves (FPLAPW) method, the exchange–correlation energies local spin density approximation (LSDA) [16,17], Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) [18], modified Becke-Johnson potential (mBJ) [19], generalized gradient approximation with Hubbard U (GGA + U) [20], and spin orbit coupling (GGA + U (SOC)) [21] are used.

2. Computational details

Kohn–Sham equations [22] are solved to calculate the structural, electronic and magnetic properties of the cubic perovskites $MTaO_3$ (M = Ca, Sr and Ba). The full potential linearized augmented plane waves (FP-LAPW) method [22] with the LSDA [16,17], GGA-PBE [18], mBJ [19], GGA + U [20] and GGA + U + SOC [21] are used to solve the Kohn–Sham equations. The three independent elastic coefficients are calculated using the method developed by Charpin as implemented in the WIEN2k package [23].

In the Kohn–Sham scheme the electron density are obtained by summing over all the occupied states [24]. Details of the spin-dependent FP-LAPW method, formulas and WIEN2k software used in the present calculations can be found in Ref. [23].

There are several methods to incorporate the *U*-term [25,26] but we used the self-interaction correction (SIC) introduced by Anisimov et al. [20] as implemented in WIEN2k.

An approximated correction value of $U–J$ for the SIC is probably best for strongly correlated systems [23], for a full potential method we use an "effective" $U_{eff} = U–J$ by setting J = 0.

After examining and testing several values of Hubbard potential in order to adjust the *Ta-5d* orbitals in the density of states, the final $U_{eff} = U–J = 2.0$ eV is used; as in our previous work [4].

In order to ensure that no electron leakage is taking place semi-core states are included and are described with local orbitals. To ensure well converged and accurate results 286 k points and $R_{MT} \times K_{max} = 8.00$ basis functions are used.

3. Results and discussions

3.1. Structural properties

The ground state structural properties and geometries of the cubic perovskites $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ are studied, using Birch Murnaghan equation of state [27]. The volume of each compound is optimized like in our previous work [3,4]. From the ground state volumes the equilibrium lattice constants (a_o) and ground state energies (E_0) for all the materials are evaluated. The calculated lattice constants and ground state energies of all the three compounds by LSDA, GGA, GGA + U and GGA + U (SOC) are presented in Table 1.

The lattice constants of these compounds are also analytically calculated using ionic radii in the following formula [28];

$$a_o = \alpha + \beta(r_M + r_O) + \gamma(r_{Ta} + r_O) \quad (1)$$

where α(0.06741), β (0.4905) and γ (1.2921) are constants, r_M is the ionic radii of Ca (1.34 Å), Sr (1.44 Å) and Ba (1.61 Å), r_{Ta} is the ionic radius of Ta (0.68 Å) and r_O is the ionic radius of O (1.35 Å) [29].

Verma and Jindal [30] predicted another model for the calculations of the lattice constants of the cubic perovskites based on the valance electron and ionic radii as given below;

$$a_o = K(V_M V_{Ta} V_O)^S r_{av} \quad (2)$$

where V_M, V_{Ta}, V_O are the valance electron in M, Ta and O respectively, K (2.45) and S (0.09) are the constants for cubic systems, r_{av} is the average ionic radii of $MTaO_3$ system. The lattice constants calculated using Eqs. (1) and (2) are also presented in Table 1. The comparison of the lattice constants of $MTaO_3$ (M = Ca, Sr and Ba) by DFT as well as ionic radii methods (Eq. (1)) and (Eq. (2)) with the experiments shows close resemblance. The maximum difference of 3% is observed for the analytical ionic radii methods.

In the cubic structure, Ta lies at the body center position of the cube, oxygen at face centers and M at each corner of the unit cell. Where strong covalent bond exists between Ta and O and strong ionic bond between M (M = Ca, Sr and Ba) and Ta. The bond lengths between different atoms are also calculated and are presented in Table 1. The bond length between M and O is increases, as we go from Ca → Sr → Ba. This increase is due to the larger size of Ba than Sr and Ca as shown in Fig. 1. A similar trend is also observed for the bond length M—Ta. Bond lengths can be used to estimate tolerance factor (t) of perovskites, which is an important parameter, describes symmetry of these compounds. Tolerance factor of these compounds are calculated on the basis of bond lengths between different bonds in these compounds using the following formula [28]:

$$t = \frac{0.707(\langle M-O\rangle)}{(\langle Ta-O\rangle)} \quad (3)$$

where $\langle M–O\rangle$ and $\langle Ta–O\rangle$ are the average bond lengths between M and O and Ta and O respectively.

The tolerance factor (t) can also be found using the well known Goldschmidt's, formula from the ionic radii in these unit cells [31];

$$t = \frac{0.707(r_M + r_O)}{(r_{Ta} + r_O)} \quad (4)$$

The evaluated results obtained through these relations (Eq. (3) and Eq. (4)) are compared with each other in Table 1. It is clear from the table that our calculated tolerance factors by both methods are in the range of cubic phase (0.93–1.04) [32], which theoretically confirm the experimental cubic structure of these compounds.

3.2. Mechanical properties

Elastic properties and elastic constants of a material explain most of the mechanical properties and response of the crystal to external forces such as mechanical stability, strength, acoustic phonon frequencies, Debye temperature, ductile or brittleness

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072

Table 1
Calculated DFT, experimental and analytical results of the lattice constants (a_o), ground state energies (E_o), tolerance factors (t) and bond lengths of $MTaO_3$ (M = Ca, Sr and Ba).

Compound	GGA	LSDA	GGA + U	GGA + U (SOC)	Exp.	I.R method	V.E method
$CaTaO_3$							
a_o (Å)	3.975	3.954	3.99	3.98	3.88[a]	4.00	3.90
E_o (Ry)	−33061.505	−33040.794	−33052.629	−33053.965			
t	0.99						
Bond lengths							
Ca–O (Å)	2.8106						
Ca–Ta (Å)	3.4423						
Ta–O (Å)	1.9874						
$SrTaO_3$							
a_o (Å)	4.007	3.99	4.03	4.02	3.97[b]	4.06	4.02
E_o (Ry)	−38059.975	−38035.661	−38049.451	−38049.777			
t	0.99					0.97	
Bond lengths							
Sr–O (Å)	2.8334						
Sr–Ta (Å)	3.4701						
Ta–O (Å)	2.0035						
$BaTaO_3$							
a_o (Å)	4.057	4.038	4.08	4.07	–	4.16	4.21
E_o (Ry)	−47978.502	−47949.565	−47965.944	−47966.288			
t	0.99					1.03	
Bond lengths							
Ba–O (Å)	2.8687						
Ba–Ta (Å)	3.5135						
Ta–O (Å)	2.0285						

[a] [12].
[b] [13].

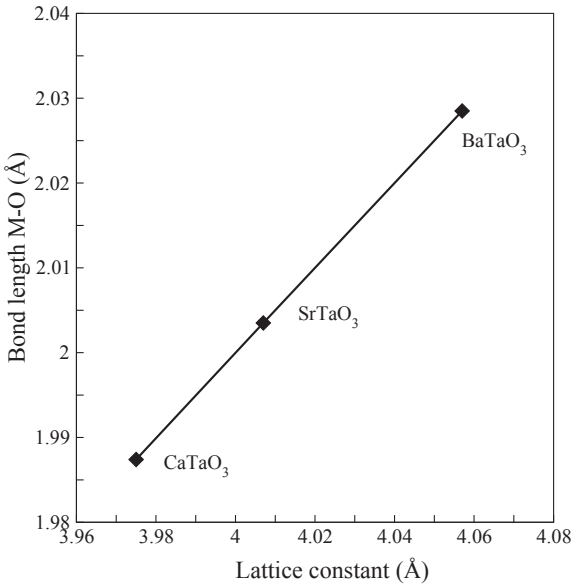


Fig. 1. Lattice constants versus change in bond lengths between M and O of $MTaO_3$ (M = Ca, Sr and Ba).

behavior [33]. These properties are based on the analysis of independent elastic stiffness coefficients (C11, C12, C44), bulk modulus B, Young's modulus Y, shear modulus G, and anisotropy factor A. First principle calculations are carried out for the independent elastic constants Cij, whereas the remaining constants are determined by using these three elastic parameters. The calculated elastic constants at ambient pressure for $MTaO_3$ (M = Ca, Sr and Ba) perovskites are listed in Table 2. Due to the unavailability of measured data in the literature, these elastic constants are not compared. The table shows that these compounds satisfy mechanical stability criteria $C_{11}-C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2\,C_{12} > 0$ [34], and also satisfy the cubic stability condition i.e. $C_{12} < B < C_{11}$ [12].

Table 2
Calculated elastic constants *Cij* (GPa), bulk modulus *B* (GPa), Voigt's G_V, Reuss's G_R, and Hill's Shear modulus *G* (GPa), Young's modulus *Y* (GPa), Poisson's ratio υ, anisotropy constant *A*, Cauchy pressure *C″* and *B/G* ratio of the cubic $MTaO_3$ (M = Ca, Sr and Ba).

Parameters	$CaTaO_3$	$SrTaO_3$	$BaTaO_3$
C_{11}	404.32	285.56	490.55
C_{12}	86.241	74.481	117.00
C_{44}	16.656	34.487	81.00
B	192.27	144.84	241.52
G_V	73.612	62.91	123.31
G_R	25.954	47.20	104.72
G	49.78	55.05	114.01
Y	195.84	164.86	316.13
υ	0.3302	0.3103	0.2818
A	0.1047	0.3268	0.4336
C'	69.58	39.99	36.00
B/G	3.8624	2.6311	2.1184

This means that these compounds are mechanical stable in the cubic phase at ground state.

The Voigt–Reuss–Hill (VRH) method [35–37] is used to describe bulk modulus (B) shear modulus (GH). Both bulk and shear modulus are used as a measure of the hardness of materials. From the table, $SrTaO_3$ has a smaller value of the bulk and shear modulus whereas $BaTaO_3$ has larger values, which confirms that $BaTaO_3$ is harder material than the rest compounds. Covalently bonded compounds generally have high shear modulus. The Young's modulus (Y) is key parameter for engineering and technological point of view. It is the ratio of stress and strain, and measure stiffness of the material. Larger is the value of Y, stiffer is the material, and stiffer solids have covalent bonds nature [38]. The table shows that $BaTaO_3$ has a highest value of Y, implying more covalent bond nature as compare to other two compounds. To measure the anisotropy of elastic wave's velocity and structural stability of a material, the anisotropic factor A is used. For isotropic materials, the value of anisotropic factor is unity. Introducing of micro crakes in a material can be related to anisotropic factor. The calculated elastic anisotropic factor for $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ is less than

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072

1, which indicates that these compounds are not elastically isotropic. The nature of the bond of cubic systems can also be explained in terms of their Cauchy pressure (C12−C44). Materials with positive Cauchy pressure are considered to have metallic bond, whereas negative Cauchy pressure means bond is angular in character [39]. The calculated Cauchy pressures for $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ are positive, which confirm their ductile nature. According to the Pugh's ratio, the high B/G ratio is associated with the ductile and the low ratio is associated with the brittle nature of the materials. To separate the ductile and brittle, the critical number is found to be 1.75 [40]. From the present of B/G ratio for $CaTaO_3$ show more ductile nature while $SrTaO_3$ and $BaTaO_3$ show less ductile nature.

3.3. Electronic properties and density of states

To study the electronic properties of $MTaO_3$ (M = Ca, Sr and Ba) the spin dependent electronic band structures of these compounds are calculated by LSDA, GGA, mBJ, GGA + U and GGA + U (SOC) and are presented in Fig. 2 (a), (b) and (c). It is clear from the plots that the band structures of these compounds by different exchange correlations potentials are similar with a small difference in details. Furthermore, the profiles are identical for up and down spins for each compound. The plots also reveal that the conduction band minima are pulled by the valance band. These bands cross the Fermi level; make these compounds metallic. The gap in the valance band sharply decreases in the sequence $CaTaO_3 \rightarrow SrTaO_3 \rightarrow BaTaO_3$. To reveal the origin of the electronic band structure the total and partial densities of states of these compounds are calculated and presented in Figs. 3 and 4. It is also clear from the figures that the total and partial densities are identical for both spins for all the compounds and hence no spin polarization is observed predominantly. The total and partial densities of states for $CaTaO_3$ are shown in Fig. 3 and by LSDA, GGA, mBJ, GGA + U and GGA + U (SOC). The densities calculated by LSDA and GGA are almost identical with a small difference in details, while mBJ, GGA + U and GGA + U (SOC) is different in which the d-state of Ta is localized. These potentials handle the exchange correlation effect for the highly correlated electron systems (partially filled d and f-orbitals), which not only provides better results, closer to experiments, but also the correct band dispersion of the highly correlated electrons system.

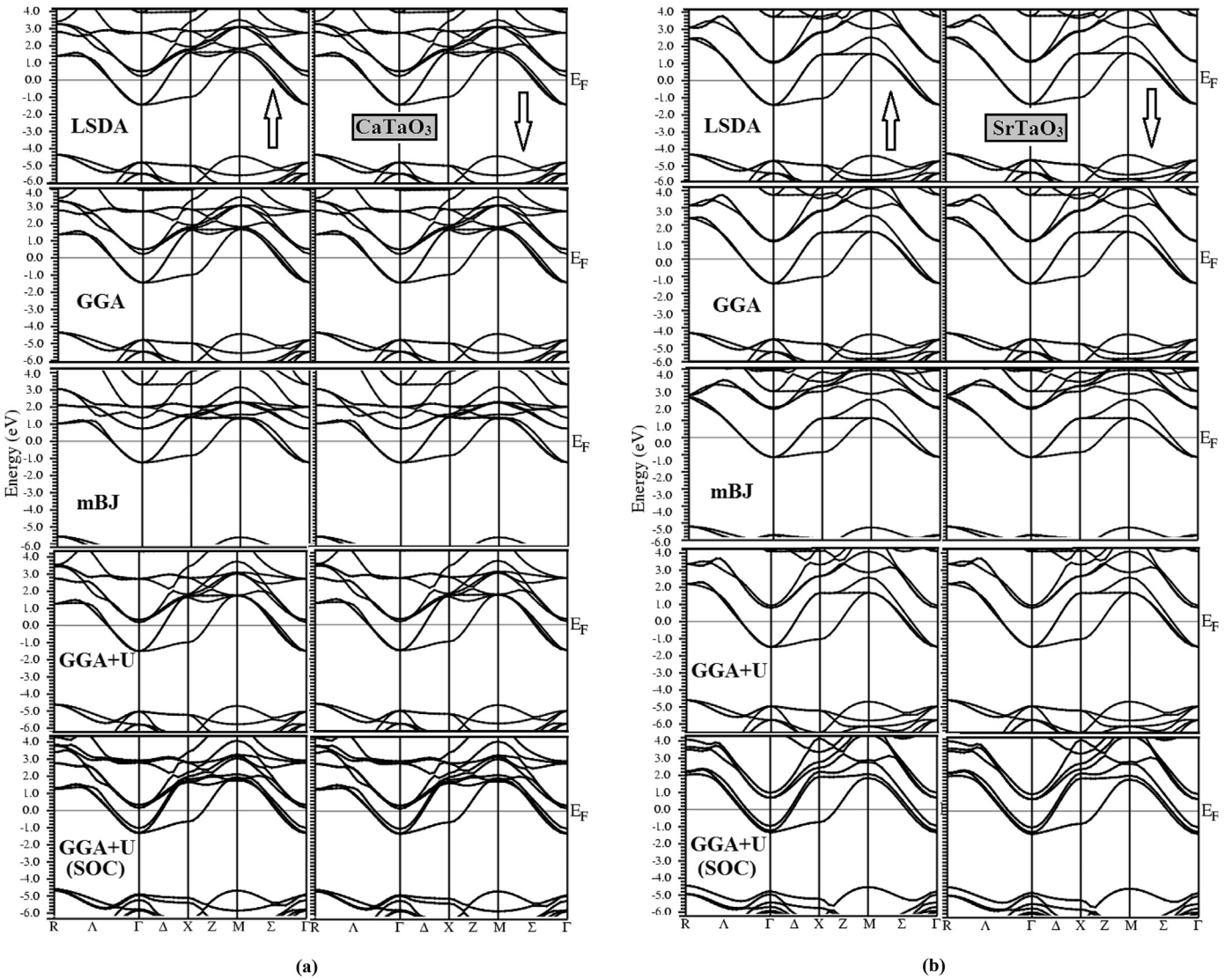
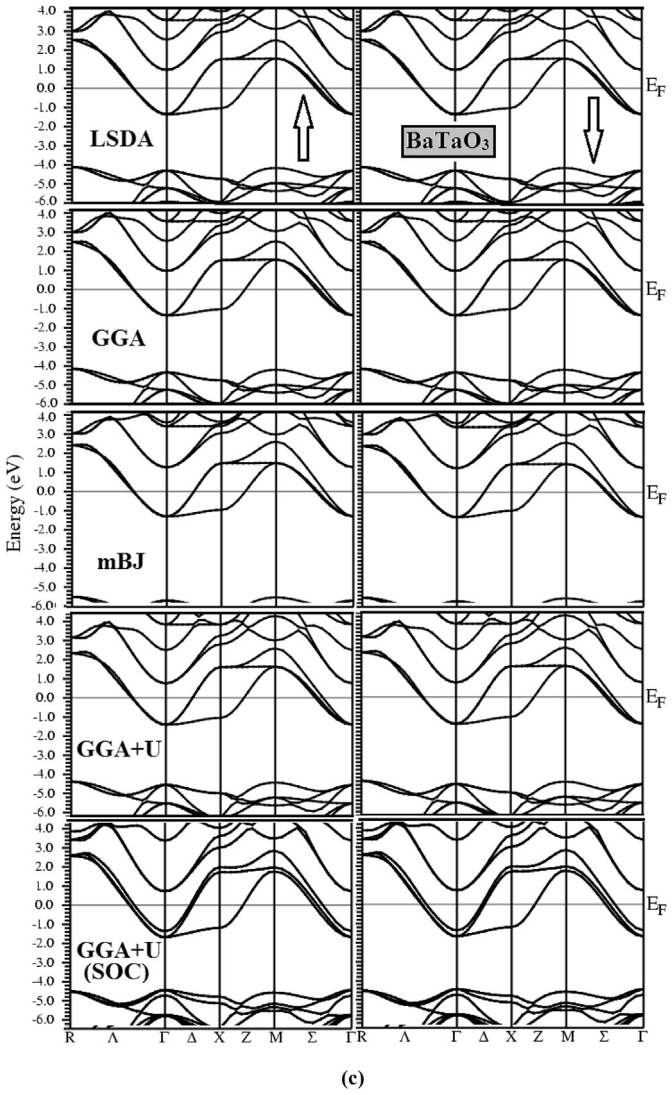


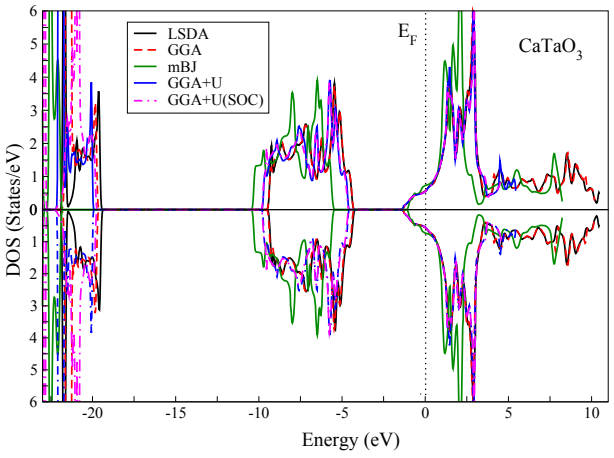
Fig. 2. Spin dependent electronic band structures of (a) $CaTaO_3$, (b) $SrTaO_3$ and (c) $BaTaO_3$ by LSDA, GGA, mBJ, GGA + U and GGA + U (SOC).

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072

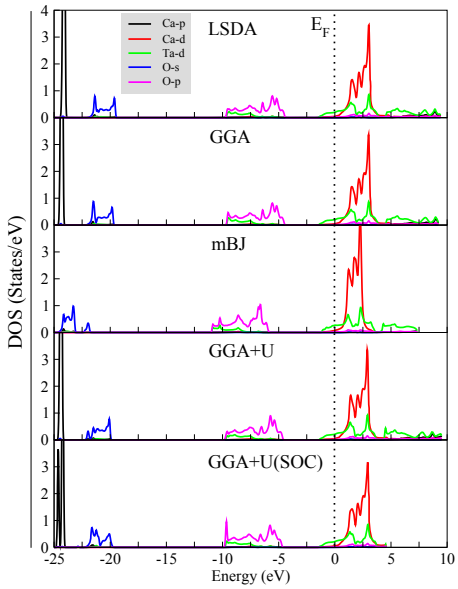


(c)

Fig. 2. (*continued*).



(a)



(b)

Fig. 3. Spin dependent (a) total and (b) partial DOS of the $CaTaO_3$ by LSDA, GGA, mBJ, GGA + U and GGA + U (SOC).

The DOSs are divided into three regions; the first region ranges from −22 eV to −19.5 eV is due to the O-2s state, the second region ranges from −9.4 to −4.3 eV is core of the valance band is mainly contributed by the 2p state of O and the third region is spread over −1.4–10 eV, is conduction band. Conduction band minimum is pulled by the valance band which crosses the Fermi level and enter into the valance band up to 1.4 eV. The figure shows that the maximum contribution around the Fermi level is of Ta-5d states. The first peak in the conduction band at 1.5 eV is due to Ta-5d-state and maximum peak at 2.8 eV is due to unoccupied 3d states of Ca. It is clear from the Fig. 3(b) (partial density of states) that a small change occurs in the densities by mBJ, GGA + U and GGA + U (SOC) in which the d-state of Ta localized. Ta-5d states occur at Fermi level makes the compound metallic. Hence $CaTaO_3$ is metallic for both spins.

Fig. 4 (a) and (b) show spin dependent total and partial density of states for $SrTaO_3$. It is clear from the figure that the bottom of the valance bands occurs from −22 to −18.1 eV which is fully occupied by O-2s and Sr-3p states. The intermediate region in the valance band ranges −9.4 to −4.2 eV. The main contribution in this region is due to the 2p states of O and maximum peak occurs at −5.4 eV. Top region spreads from −1.4–10 eV, just like $CaTaO_3$ in $SrTaO_3$ the Ta-5d state of the conduction band crosses the Fermi level and enters into the valance band up to 1.4 eV, makes the compound metallic. In conduction band peak at 1.5 eV is due to 5d-states of Ta, maximum peak at 5 eV is due to the unoccupied 4d states of Sr. The partial density of states presented in the figure reveal that the hybridization between Ta-5d and O-2p states at the Fermi level makes $SrTaO_3$ metallic for both spins. A similar to $CaTaO_3$ and $SrTaO_3$ trend for the total and partial densities of states for $BaTaO_3$ is observed, with a small difference in details, where the conduction bands crosses the Fermi level and enters into the valance band up to −1.3 eV (figure not given). Hence all the three compounds are metals.

Furthermore to check the electrical conductivity of these compounds BoltzTraP code [41] is utilized. The plot between electrical conductivity by time factor (σ/τ) versus temperature is shown in Fig. 5. At 150 K $CaTaO_3$ and $BaTaO_3$ posses high conductivity of the order of 4×10^{22} $(ohm.m)^{-1}$/sec, while the conductivity of $SrTaO_3$ is 0.35×10^{22} $(ohm.m)^{-1}$/sec. The electrical conductivity of $CaTaO_3$ and $BaTaO_3$ decreases exponentially as temperature increases; whereas this decrease for $SrTaO_3$ is almost linear. All the three compounds show significant electrical conductivity up to 400 K

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072

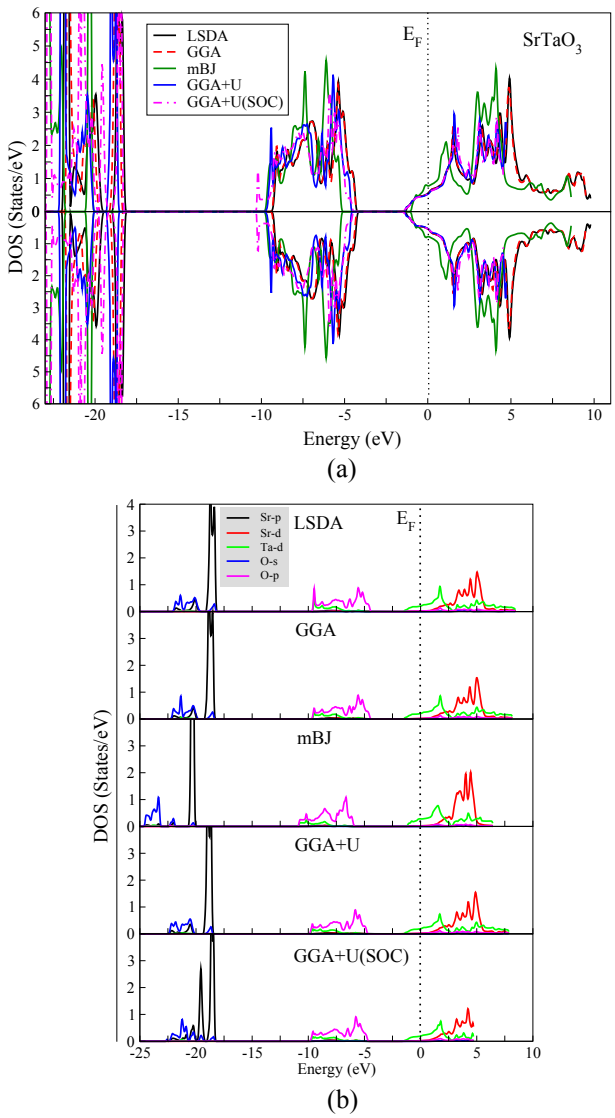


Fig. 4. Spin dependent (a) total and (b) partial DOS of $SrTaO_3$ by LSDA, GGA, mBJ, GGA + U and GGA + U (SOC).

$SrRuO_3$ has been investigated as an electrode material because of its metallic character [42] and has electrical resistivity of the order of 2×10^{-4} Ω cm [11]. The results obtained like metallic nature and electrical conductivity are identical with $SrRuO_3$ and $CaRuO_3$ hence it is expected that $MTaO_3$ (M = Ca, Sr and Ba) could be used as efficient electrode materials.

3.4. Magnetic properties

Magnetism in condensed matter arises due to a combination of the individual atoms and the crystal structure of the solids. At the atomic level, magnetism is contributed by the movements of electrons, originated from orbital and spins motion. In atoms the orbital moments of electron pairs point in opposite directions canceling each other, same is true for the spin moments. The overall magnetic moment of the atom is thus the sum of all of the magnetic moments of the individual electrons, accounting for moment cancellation between properly paired electrons. For the case of a completely filled electrons shell, the magnetic moments completely cancel out each other. Thus only atoms with partially filled electron shells have magnetism [43,44].

To study the ground state magnetic properties of $MTaO_3$ (M = Ca, Sr and Ba) perovskites we optimized the double cell of each compound for paramagnetic, ferromagnetic and anti-ferromagnetic phases as shown in Fig. 6. The anti-ferromagnetic configuration is calculated by accounting it in double cell one Ta is being spin up (↑) and the other is spin down (↓) states, while for ferromagnetism the spins are parallel like our previous work [3,5]. The ground state energies curves for all the three compounds are plotted in Fig. 7. It can be seen from the figure that all the three compounds lower their ground state energies in paramagnetic phase. Hence all the three compounds are paramagnetic in nature. For the complete description of magnetic moments in these compounds we calculate the spin and orbital's moments.

GGA + U (SOC) self consistent field calculations are performed in order to investigate the magnetic moments of $MTaO_3$ (M = Ca, Sr and Ba), like spin magnetic moments in the interstitial region, spin and orbital magnetic moments inside muffin-tin sphere of Ca, Sr and Ba, Ta and O atoms. The magnetic moments at interstitial site for $CaTaO_3$ 0.0362 μ_B, for $SrTaO_3$ 0.10256 μ_B and for $BaTaO_3$ are 0.04607 μ_B respectively. The orbital magnetic moments inside muffin-tin spheres for Ca, Sr and Ba are 0.00149 μ_B, 0.00149 μ_B and 0.00255 μ_B respectively, while the spin moments are −0.00148 μ_B, −0.00148 μ_B and −0.00255 μ_B. The negative sign of the spin magnetic moments show the opposite alignment to other moments which completely cancel the orbital effect of Ca, Sr and Ba. The orbital magnetic moments of Ta in these materials are 0.06486 μ_B, 0.06517 μ_B and 0.06862 μ_B, while the spin moments are −0.06509 μ_B, −0.06568 μ_B and −0.06903 μ_B in $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ cells, respectively and opposite are in alignments.

The orbital magnetic moments of O(1) are 0.00043 μ_B, 0.00061 μ_B and 0.00065 μ_B and the spin moments are −0.00043 μ_B, −0.00061 μ_B and −0.00065 μ_B respectively. Here the negative sign of orbital moments show opposite alignment to orbital moments which completely cancel the effect of each other result zero net magnetic moments. A similar trend is observed for O(2) × 2 oxygen atom in these compounds with a small difference in detail. The total magnetic moments of these compounds is due to the contribution from the different sites of the atoms like interstitial magnetic moments, total orbital and total spin magnetic moments. The net magnetic moment of $CaTaO_3$ is 0.00232 μ_B, and for $SrTaO_3$ 0.00222 μ_B and for $BaTaO_3$ is 0.00147, which decrease as we going from $CaTaO_3$ to $BaTaO_3$. Our calculated results show that the directions of the total magnetic moment as well as orbital moments of Ta and M are opposite to spin moments for all the three compounds result weak net magnetic moments.

The weak magnetic response of these materials is due to the partial unpaired electrons effect in these compounds and is responsible for the paramagnetic behavior. Hence, the ground state energy, symmetric densities of states and negligible magnetic moments confirm the paramagnetic nature of these perovskites. Based on the above properties metallic paramagnetic nature it is expected that these perovskites could be used as efficient electrodes materials.

4. Conclusions

In summary ground state structural, elastic, electronic and magnetic properties of the cubic perovskites $CaTaO_3$, $SrTaO_3$ and $BaTaO_3$ have been investigated by using LSDA, GGA, mBJ, GGA + U and GGA + U (SOC) within the frame work of DFT. The calculated relax lattice constants by DFT and analytical ionic radii methods are consistent with the experimental results. The theoretically calculated tolerance factors and mechanical properties confirm that these compounds are ductile, stable in the cubic phase and confirm that $BaTaO_3$ is harder material in the entire three compounds. The

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072

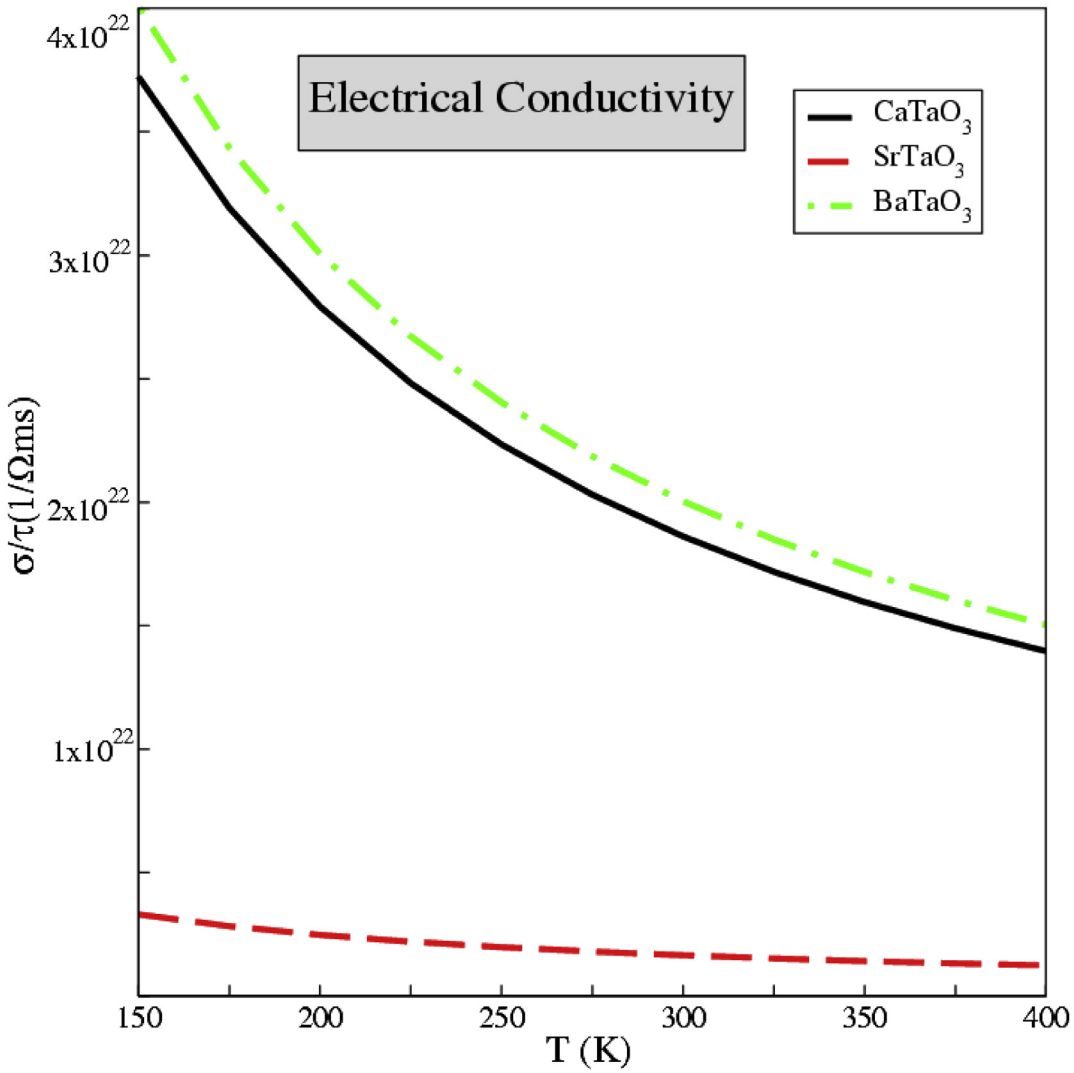


Fig. 5. Electrical conductivity versus temperature of $MTaO_3$ (M = Ca, Sr and Ba).

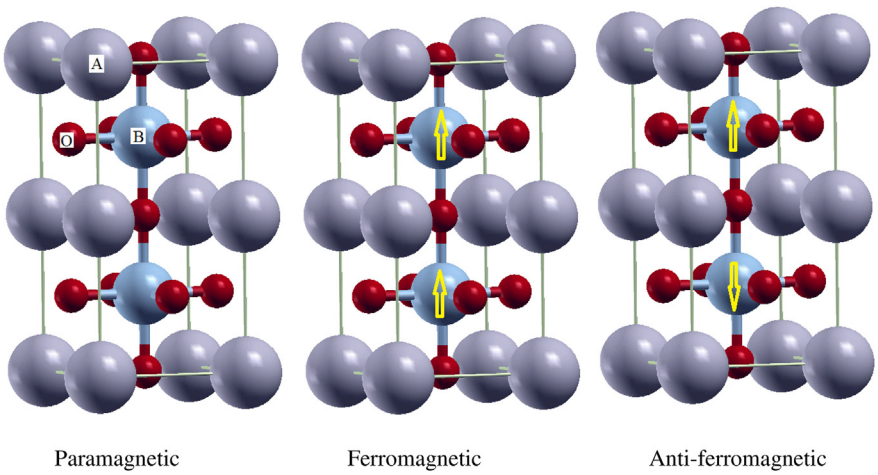


Fig. 6. Double cell crystals of $MTaO_3$ (M = Ca, Sr and Ba) for paramagnetic, ferromagnetic and anti-ferromagnetic calculations.

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072

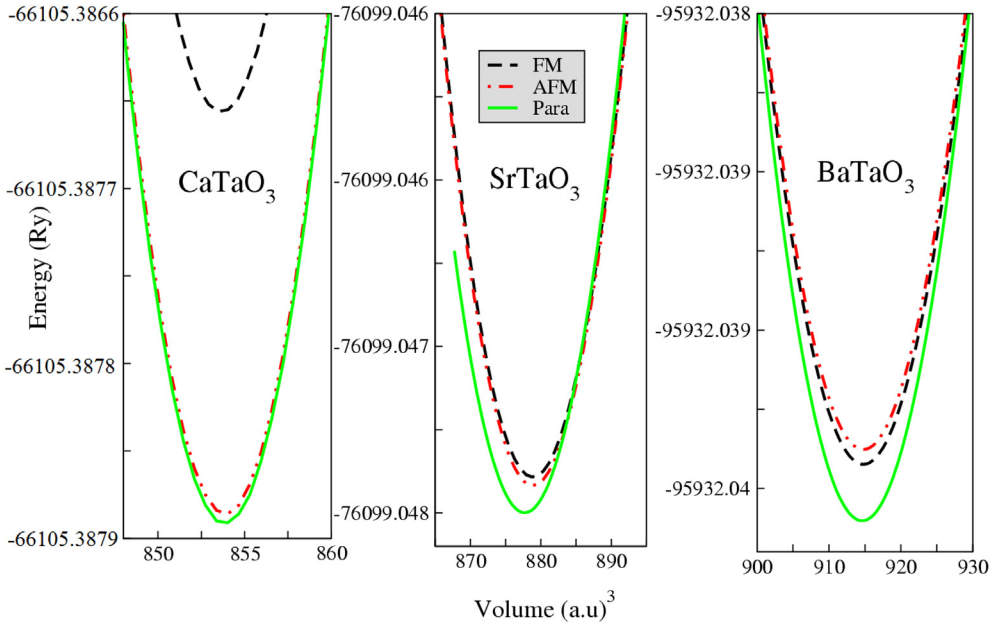


Fig. 7. Double cell optimization curves of $MTaO_3$ (M = Ca, Sr and Ba) for paramagnetic, ferromagnetic and anti-ferromagnetic phases.

spin-dependent electronic band structures, total and partial densities of states reveal that these compounds are metals. Electrical conductivity of these compounds is calculated on the basis of BoltzTraP code. The optimized ground state energy demonstrates the paramagnetic nature of these oxides. These interesting properties predict that these materials could be used as efficient electrode materials and need experimental investigations.

References

[1] Y. Moritomo, A. Asamitsu, H. Kuwahara, Y. Tokura, Nature 380 (1996) 141.
[2] J.M. De Teresa, M.R. Ibarra, P.A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A.D. Moral, Z. Arnold, Nature 386 (1997) 256.
[3] Z. Ali, I. Ahmad, I. Khan, B. Amin, Intermetallics 31 (2012) 287.
[4] Z. Ali, I. Khan, I. Ahmad, S. Naeem, H.A. Rahnamaye Aliabad, S.J. Asadabadi, D. Zhang, Phys. B 423 (2013) 16.
[5] Z. Ali, M. Shafiq, S.J. Asadabadi, H.A. Rahnamaye Aliabad, I. Khan, I. Ahmad, Comput. Mater. Sci. 81 (2014) 141.
[6] J.G. Cheng, T. Ishii, H. Kojitani, K. Matsubayashi, A. Matsuo, X. Li, Y. Shirako, J.-S. Zhou, J.B. Goodenough, C.Q. Jin, M. Akaogi, Y. Uwatoko, Phys. Rev. B 88 (2013) 205114.
[7] B.C.H. Steele, Solid State Ionics 86–88 (1996) 1223.
[8] J.W. Fergus, Solid State Ionics 177 (2006) 1529.
[9] J.B. Goodenough, Y.H. Huang, J. Power Sources 173 (1) (2007) 1.
[10] J.T.S. Irvine, Perovskite Oxide for Solid Oxide Fuel Cells, Springer, 2009, pp. 167–182.
[11] G. Koster, L. Klein, W. Siemons, G. Rijnders, J.S. Dodge, C.B. Eom, D.H.A. Blank, M.R. Beasley, Rev. Mod. Phys. 84 (2012) 253.
[12] M. Gasperin, Acta. Cryst. 11 (1958) 739.
[13] Copyright (C) M.A. Rodriguez, T.J. Boyle, B.A. Hemandez, JCPDS-International Centre for Diffraction Data, 1999.
[14] C.L. Hung, Y.L. Chueh, T.B. Wu, L.J. Chou, J. Appl. Phys. 97 (2005) 034105.
[15] K. Wakino, Ferroelectrics 91 (1989) 69.
[16] U. Barth, L. Hedin, J. Phys. C 5 (1972) 1629.
[17] J.F. Janak, Phys. Rev. B 16 (1977) 255.
[18] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[19] A.D. Becke, E.R. Johnson, J. Chem. Phys. 124 (2006) 221101.
[20] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, Phys. Rev. B 48 (1993) 16929.
[21] D.D. Koelling, B.N. Harmon, J. Phys. C. Solid State Phys. 10 (1977), 3107–31014.
[22] W. Kohn, L.S. Sham, Phys. Rev. A 140 (1965) 1133.
[23] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2K: an Augmented Plane Wave + Local Orbital Program for Calculating Crystal Properties, Techn Universitat, Wien, Austria, 2001.
[24] K. Schwarz, J. Solid State Chem. 176 (2003) 319.
[25] A.G. Petukhov, I.I. Mazin, Phys. Rev. B 67 (2003) 153106.
[26] P. Novak, J. Kunes, L. Chaput, W.E. Pickett, Phys. Status Solidi B 243 (2006) 563.
[27] F. Birch, Phys. Rev. 71 (1947) 809.
[28] Z. Ali, I. Ahmad, B. Amin, M. Maqbool, G. Murtaza, I. Khan, M.J. Akhtar, F. Ghaffor, Phys. B 406 (2011) 3800.
[29] A. Majid, Y.S. Lee, Adv. Inform. Sci. Serv. Sci. 2 (2010) 175.
[30] A.S. Verma, V.K. Jindal, J. Alloy Comp. 485 (2009) 514.
[31] V.M. Goldschmidt, Geochemistry, Oxford University Press, Oxford (, 1958.
[32] N. Xu, H. Zhao, X. Zhou, W. Wei, X. Lu, W. Ding, F. Li, J. Hydrog. Energy 35 (2010) 7295.
[33] Y. Pan, W.T. Zheng, W.M. Guan, K.H. Zhang, X.F. Fan, J. Solid State Chem. 207 (2013) 29.
[34] J. Wang, S. Yip, S.R. Phillpot, D. Wolf, Phys. Rev. Lett. 71 (1993) 4182.
[35] R. Hill, Proc. Phys. Soc. Lond. A 65 (1952) 349.
[36] W. Voigt, Ann. Phys. 38 (1889) 573.
[37] A. Reuss, Z. Angew, Math. Phys. 9 (1929) 49.
[38] C. Jenkins, S. Khanna, A Modern Integration of Mechanics and Materials in Structural Design, Mech. Mater, Elsevier, 2005, 978-0-12-383852-0.
[39] D.G. Pettifor, Mater. Sci. Technol. 8 (1992) 345.
[40] S.F. Pugh, Philos. Mag. 45 (1954) 823.
[41] G.K.H. Madsen, D.J. Singh, Comput. Phys. Commun. 175 (2006) 67.
[42] C. Santi, T. Jarlborg, J. Phys. Conden. Matter 9 (1997) 9563.
[43] S. Blundell, Magnetism in Condensed Matter, Oxford University Press, New York, 2001.
[44] M. Getzlaff, Fundamentals of Magnetism, Springer, Berlin Heidelberg, New York, 2008.

Please cite this article in press as: Z. Ali, et al., Theoretical studies of the paramagnetic perovskites $MTaO_3$ (M = Ca, Sr and Ba), Materials Chemistry and Physics (2015), http://dx.doi.org/10.1016/j.matchemphys.2015.05.072