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ATiO$_3$ (A = Ca, Sr, Ba & BP) Pervoskites in Cubic and Tetragonal Phase using TB-LMTO-ASA Method

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***Abstract:** Ground state properties of ATiO$_3$ (A = Ca, Sr, Ba & Pb) pervoskite structures in cubic and tetragonal phase were studied by tight binding linear muffin-tin orbital (TB-LMTO) method in the framework of density functional theory (DFT) with the atomic-sphere approximation (ASA). The total energy of all the compounds come under the above said structures have shown that the cubic phase is the stable structure in the ambient condition. Among these pervoskites maximum bulk modulus was obtained for BaTiO$_3$. Direct (cubic) and indirect (tetragonal) band gap was observed from the band structure calculations and the values fall within the range of 1.5 – 1.7 eV. Electron distribution of each element in the valence and conduction bands was clearly obtained from the density of states (DOS) and partial density of states (PDOS) for all the compounds. The magnetization values were found in the range of 0.4 – 0.56 x 10-5μB. The'd' orbital position of Ti was observed for all the ABO$_3$ compounds and shifted away from the Fermi level except for Ti in BaTiO$_3$. The refractive indices of the pervoskites were calculated from the energy band gap and the value is above 3 for all the compounds.*

***Keywords-** ATiO$_3$ pervoskites (A = Ca, Sr, Ba & Pb); Band structure and density of states; Refractive index and ferromagnetism; Tight Binding Linear Muffin-Tin Orbital Method.*

I. INTRODUCTION

Ferroelectrics have wider applications in pyroelectronic detectors, imaging devices, optical memories, modulators, and deflectors. Pervoskite materials are an important group of ferroelectrics [1]. The perfect pervoskite structure is cubic with a general formula ABO$_3$, where A is a divalent or monovalent metal and B is a tetra- or pentavalent atom. Basically, there are three main features in ABO$_3$ pervoskites [2]. In the first kind, the corner linked "O" atoms in the octahedral arrangements with a minor distortion are treated as rigid units to a first approximation. Secondly, inside the octahedron appears the off-centered B-cation which is associated with the phenomenon of ferro or anti-ferroelectricity. The sense of displacement in one-octahedron by way of one corner displacement of the B-cations give rise to a chain of diploes; two corner displacements produce a sheet of dipoles and three corner displacements lead to a single three-dimensional dipole [3]. Thirdly, the octahedron may tilt in a variety of configurations and have a considerable effect on the lattice parameters. Titanates, ATiO$_3$, where A = Ca, Sr, Ba, and Pb, exhibit different ferroelectric behaviours. It is known that CaTiO$_3$ and SrTiO$_3$ are incipient ferroelectrics, whereas BaTiO$_3$ and PbTiO$_3$ are well known ferroelectrics with three phases (tetragonal, orthorhombic, and rhombohedral) for BaTiO$_3$ and one tetragonal phase for PbTiO$_3$[4].

Investigations have been carried out on BaTiO$_3$ to study the structural, dielectric, elastic, and thermal properties [5]. Moreover, the infrared [6] and the Raman [7] as well as electron-spin resonance [8] spectra of BaTiO$_3$ were also studied in detail. Investigations on SrTiO$_3$ have been carried out to study the structural [9-12], dielectric [13], optical [14] and elastic [15] properties. Infrared [16, 17] and electron paramagnetic resonance [18] spectra of SrTiO$_3$ were also studied in detail. Various properties of SrTiO$_3$ have also been investigated in earlier studies [19-24]. Semi empirical MO calculations on a series of ATiO$_3$ (A = Ca, Sr, and Ba) pervoskites showed that the bare force constant for BaTiO$_3$ is smaller than that of CaTiO$_3$ and SrTiO$_3$ [25]. Local distortions exist even in cubic BaTiO$_3$ and PbTiO$_3$. On the other hand, SrTiO$_3$, which has a structure very similar to that of BaTiO$_3$, has no local distortion [26]. The above said compound having structure like pervoskite molecule, which has for first-principles band structure calculations. Also, there is less work focus on the magnetic properties ABO$_3$ pervoskites. In this paper, we have chosen four most common ferroelectric materials and calculate their magnetic properties using tight-binding linear muffin tin orbital (TB- LMTO) method within the Atomic Sphere Approximation. They are compared among each other and the refractive indices are calculated in the light of confirming their application in anti-reflecting coating application.

II. COMPUTATIONAL DETAILS

A series of ATiO$_3$ (A = Ca, Sr, Ba and Pb) pervoskite ferroelectric structures are chosen for the present study and the available structural parameters are taken from the literature [27]. We present here the electronic structures and calculations of their magnetic properties using TB- LMTO method. The accuracy of the total energies obtained within the density functional theory, using local spin density approximation (LSDA), in many cases is sufficient to predict which structure at a given pressure has the lowest free energy. Empty sphere approach is introduced in all the cases in order to keep the overlap of atomic spheres within 16%. Band dispersions and density of states (DOSs) are obtained in each case.

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The calculations are done within the ASA. For barium, the value of lmax = 3 and for titanium and oxygen lmax value is 2. Solving a Schrodinger-like Kohn- Sham equation, the radial part of the basis is obtained. Brillouin-zone integration has been utilized using the tetrahedron method with a mesh of about 500 symmetry- reduced points. In Barium molecule, 6p orbital and in the oxygen molecule 3s and 3d orbital's are having down folded and the overlap (O) matrices, dimension of the Hamiltonian (H) are do not contribute. But carry a charge. The ghost bands appearances has been prevented by the down folding.

III. RESULTS AND DISCUSSIONS

Structural Properties

In the structural optimization, the total energies as a function of reduced volume is found from theoretical calculations for the four $ATiO_3$ (A = Ca, Sr, Ba and Pb) pervoskites of cubic and tetragonal phase. The total energy is fitted into the Murnaghan's equation of state [28],

$$P(V) = 1.5 B_0 [(V_0/V)^{7/3} – (V_0/V)^{5/3}] \qquad (1)$$

Where, $P = -dE/dV$ and E is the total energy obtained from the band structure calculations and V0 is the theoretically calculated equilibrium volume at ambient conditions. Total energy versus reduced volume is shown in Fig.1. From Fig.1 one can infer that the cubic phase of $ATiO_3$ is stable at ambient conditions and also our observation from calculation predicts semiconducting nature for all the pervoskite structures. After fitting the Murnaghan's equations of state, the bulk modulus of the $ATiO_3$ pervoskites are calculated. The variation of bulk modulus with ionic radius is shown in Fig.2. From the figure, the values of bulk modulus are randomly varied with respect to the ionic radius of 'A' cations and maximum value is observed for $BaTiO_3$ in both phases, which indicates the stability of the material. The ground state properties are obtained and presented in Table 1.

The band structure of $ATiO_3$ (A = Ca, Sr, Ba and Pb) pervoskites in cubic and tetragonal phase is obtained by means of LMTO – ASA method. The calculated band structure of cubic (paraelectric) and tetragonal (ferroelectric) phases in the high symmetry directions in the Brillouin zone are depicted in Figs.3 (a&b). The energy scale is in eV and the origin of energy is arbitrarily set to be at the valence band maximum. The band gap is mainly formed by the interaction between the valence band orbital of O in 'p' like states and the anti bonding conduction band orbital of Ti and A (Ca, Sr, Ba & Pb) in 's' like states. From the figure, we get bands with large dispersion and'2p' orbital's of oxygen shows nine valence bands. In cubic phase band gap, between the range of 1.5 eV to 1.7 eV, which can be separated. Whereas in tetragonal phase by the transitional d – derived conduction band, it predicts an indirect band gap with the same values. This result is better than the previous TB LMTO-ASA calculations [29]. However, the experimental band gap of 3.2 eV [30] is higher than the resulted band gap. The possibility may be due to the'd' like orbital of Ti which is deemed to be important for band gap variation owing to p-d interaction. It is believed [31] that the p-d interaction can push the 'p' orbital of oxygen upward, thereby inducing the band gap of $ATiO_3$ to become smaller. Also, the origin of the band gap this difference arises may be due to the local density approximations which misjudge the band gaps. $BaTiO_3$ valence bands in tetragonal phase are slightly changed compared to its cubic phase while other pervoskites are not showing any variation in both phases.

Electronic Properties (Density of States)

Electron distribution in an energy spectrum is described by the density of states (DOS) and can be measured using photoemission experiment [32]. The total and partial DOS spectrum of $ATiO_3$ (A = Ca, Sr, Ba & Pb) pervoskites in both phases are shown in Figs. 4(a&b). In these figures, the zero of the energy scales (the top of the valence band) is taken as the position of the Fermi level; the valence and conduction band edges near the Fermi level are quite sharp. All the structures have the same DOS spectrum in the cubic (paraelectric) phase but in the tetragonal (ferroelectric) phase, one more oxygen atom in the valence band side of the DOS spectrum makes an additional contribution. A detailed study of the partial density of states (PDOS) gives information about the contribution of different atomic states in the band structure and also their possible hybridizations. Contribution of the core level states in the valence band is by the presence of O '2p' and A (A = Ca, Sr, Ba & Pb) cations 'p' orbital's in both phases. A weak hybridization may occur in the valence band between '2p'orbital of oxygen and 'p' orbital of Ca, Sr, Ba & Pb and it lies in the energy range 5.2 eV on top of the valence band. It shows an ionic bond between oxygen and A cations. The presence of'd' orbital states in the conduction bands of all $ATiO_3$ compounds is felt except for Ba. The'd' orbital position of Ti in $BaTiO_3$ is much close to the Fermi level compared to all the other pervoskite structures. The height of the O '2p' DOS peak is much higher than that of the Ti-3d state peak in both phases. Existence of p-d hybridization is evident from this figure and it also reflects on the Ti '3d' – O '2p' covalency. The observed Ti – d orbital positions are shown in Fig.5. From the figure, Ti-d orbital position is observed to shift away from the Fermi level except for Ti in $BaTiO_3$ and the reason may be due to the contribution of d orbitals of 'A' cations in the conduction band. No shift is observed in the tetragonal phase. In order to calculate the magnetic properties, electron spin of the respective elements in each one of the pervoskite structures is aligned. The obtained value of magnetic moments is found to be less. The observed values of magnetic moment are in good agreement with the experimental results [33] and presented in Table 1.

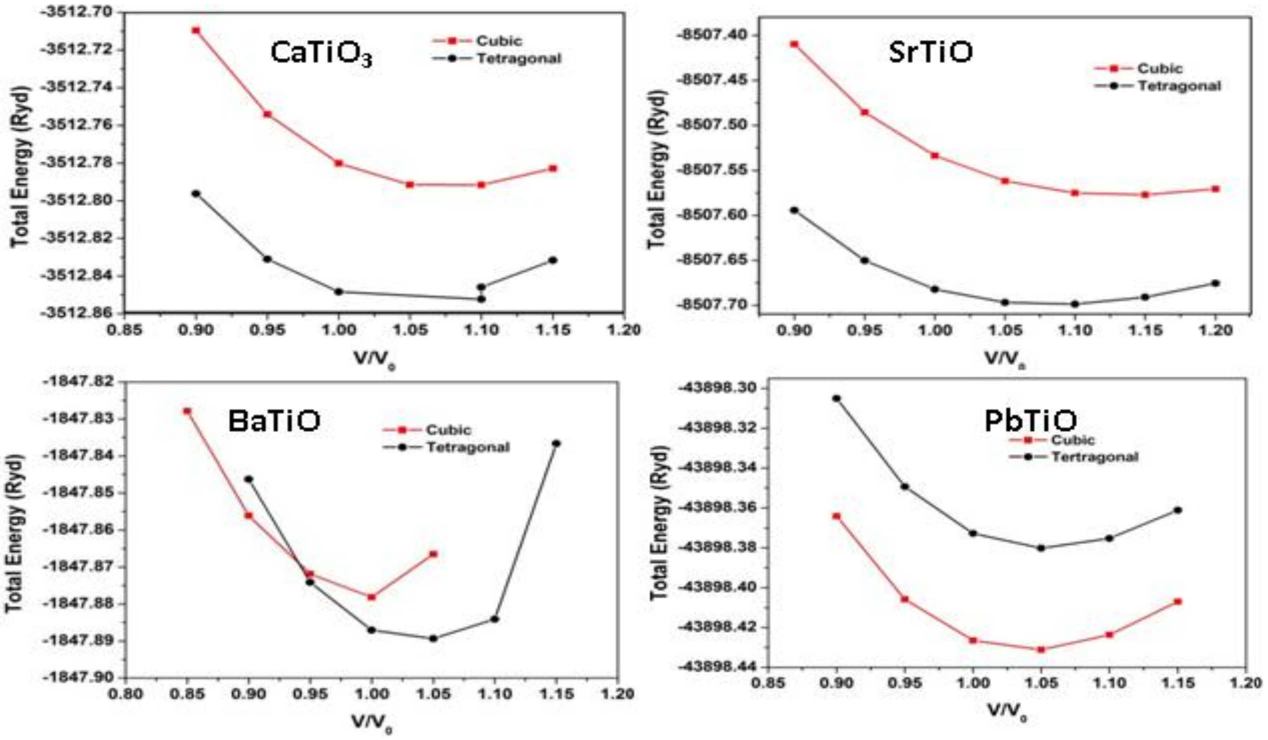

Fig.1: Total energy versus reduced volume of ATiO3 pervoskite

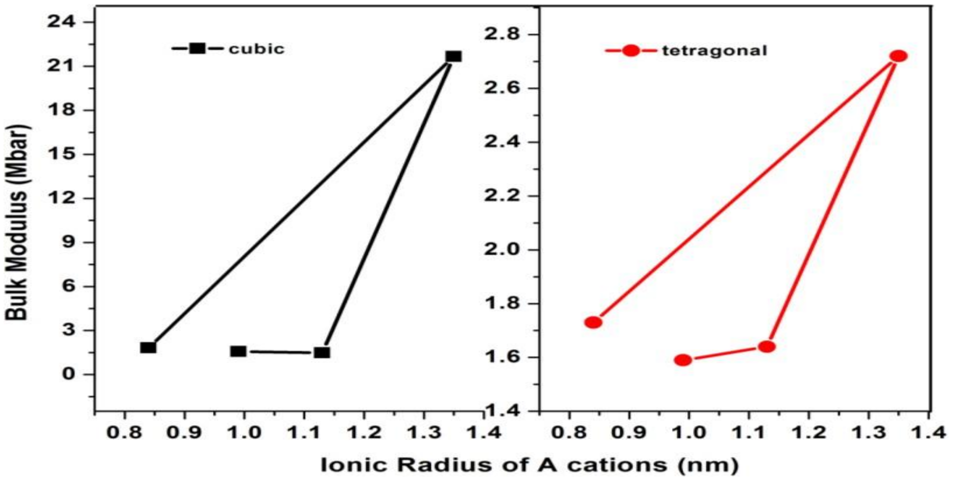

Fig.2: Variation of bulk modulus with respect to a cations ionic radius.

Table 1:

Parameters		**Cubic**				**Tetragonal**		
	$CaTiO_3$	***$SrTiO_3$***	***$BaTiO_3$***	***$PbTiO_3$***	***$CaTiO_3$***	***$SrTiO_3$***	***$BaTiO_3$***	***$PbTiO_3$***
a **(Å)**	7.49	7.69	7.50	7.60	3.83	3.88	3.99	3.90
c **(Å)**	-	-	-	-	4.14	4.05	4.036	4.15
Volume (*m^3*)	427.66	456.08	423.46	439.35	428.66	448.23	450.16	449.69
Bulk Modulus (Mbar)	1.57	1.49	21.67	1.82	1.59	1.64	2.72	1.73
Band Gap (*eV*)	1.78	1.56	1.59	1.75	1.99	1.83	1.11	1.75
Magnetization ($x10^{-5}$ μ_B)	0.38	0.45	0.52	0.56	0.42	0.41	0.56	0.52
Refractive Index (*n*)	3.044	3.088	3.082	3.05	3.002	3.034	3.178	3.05

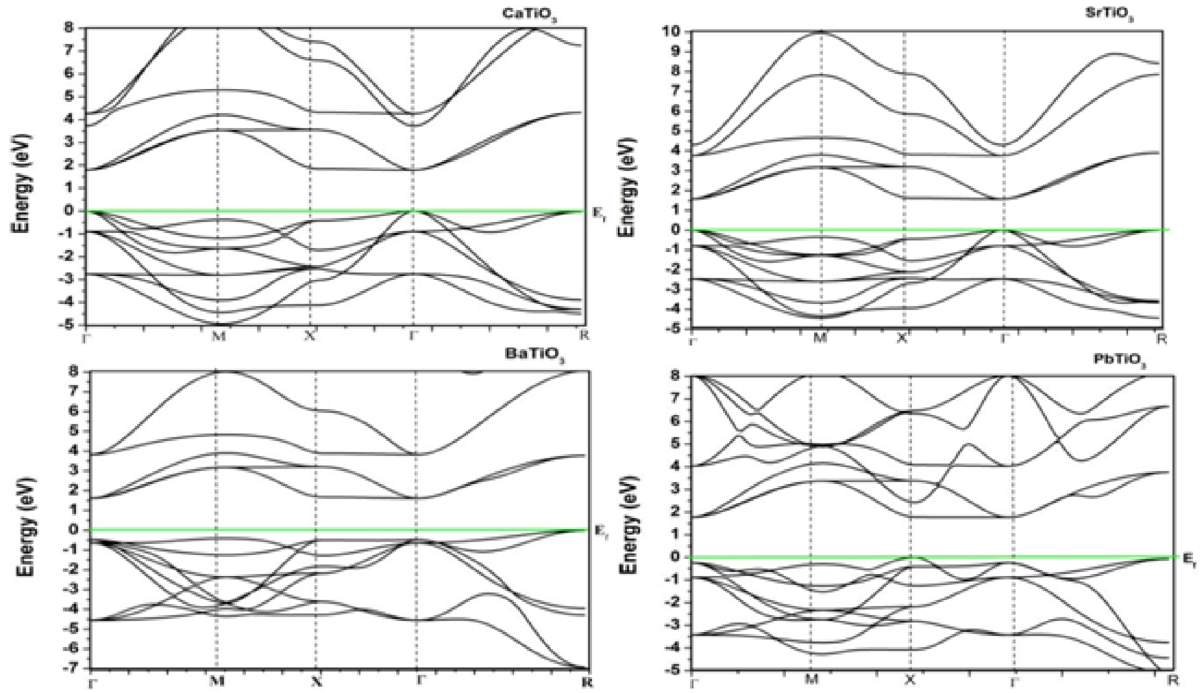

Fig.3: Band structure diagram of ATiO3 pervoskite (a) cubic.

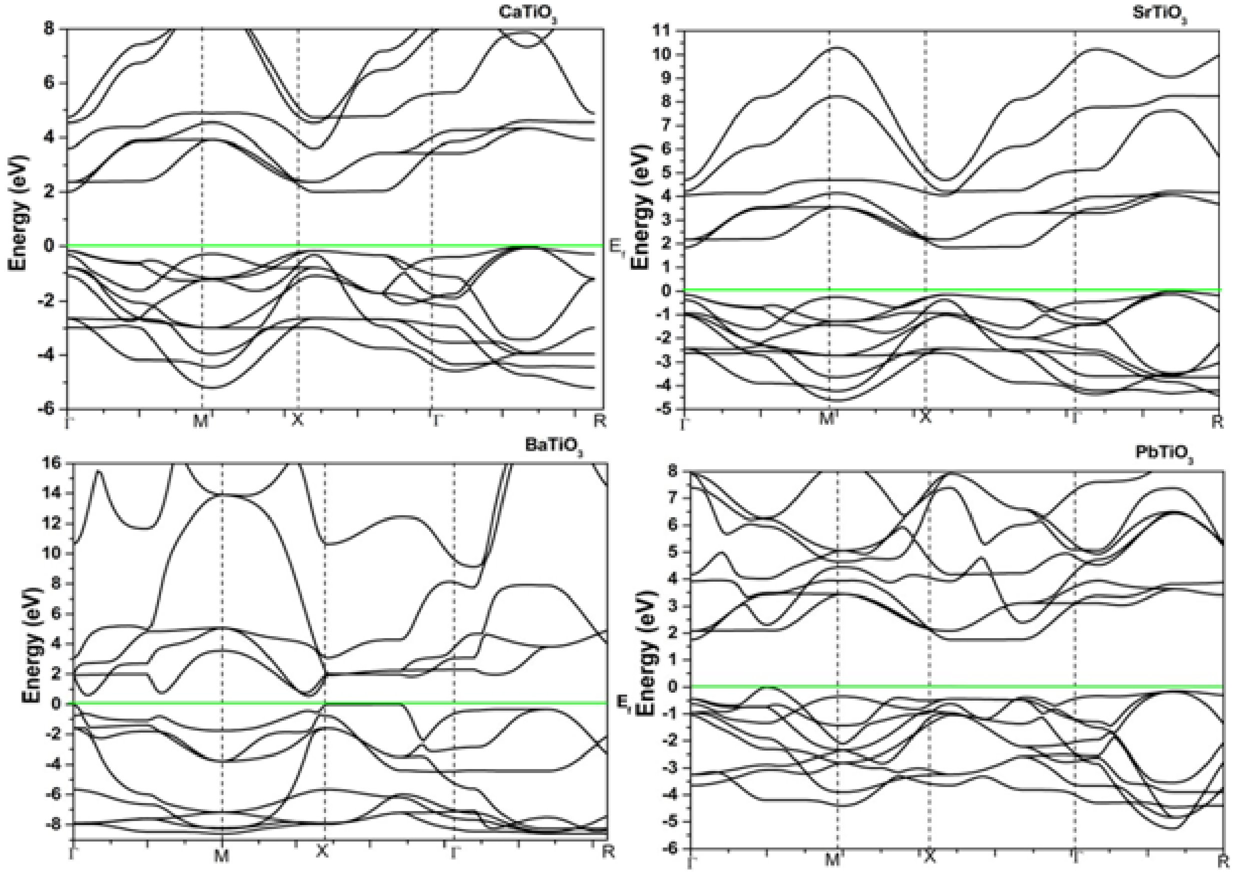

Fig.3: Band Structure Diagram of Atio3 Pervoskite (B) Tetragonal.

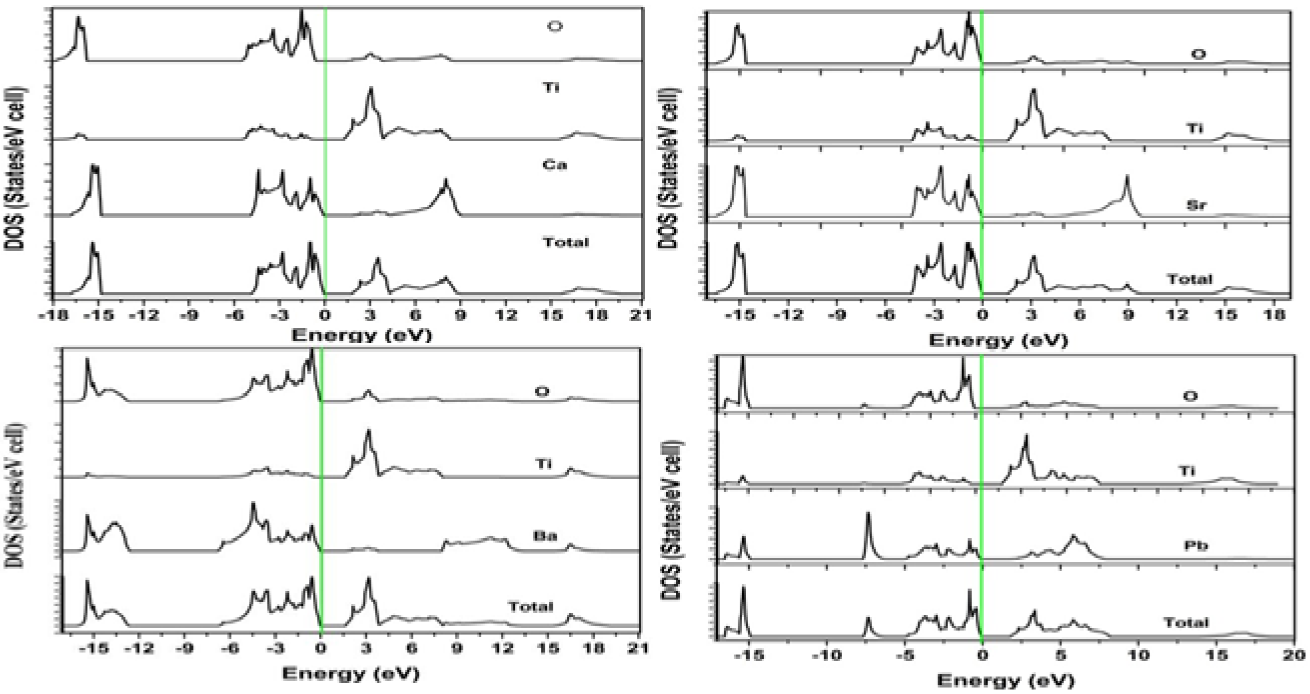

Fig.4: Density of States and Partial Density of States of Atio3 Pervoskite (A) Cubic

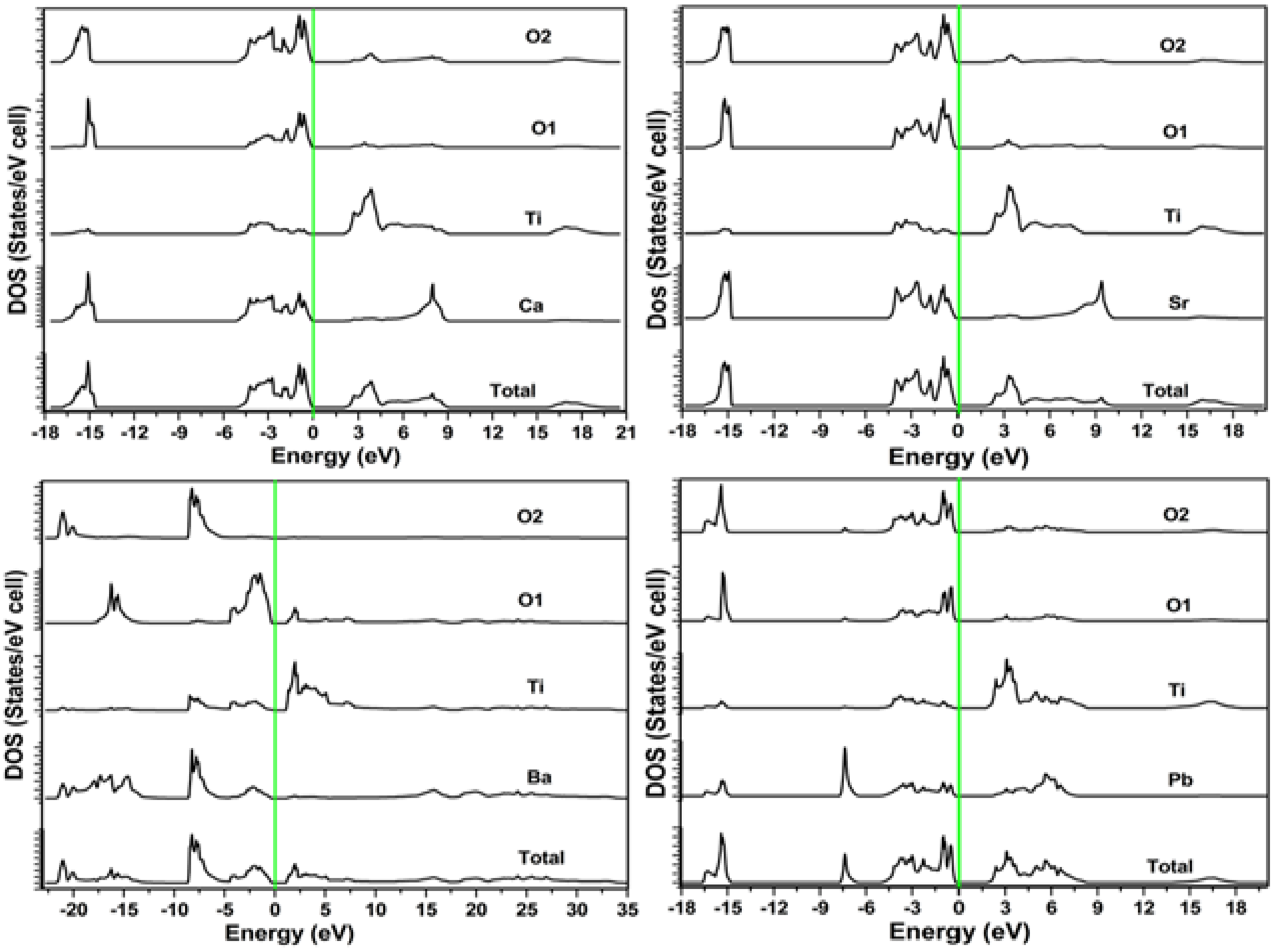

Fig.4: Density of states and partial density of states of ATiO3 pervoskite (b) tetragonal.

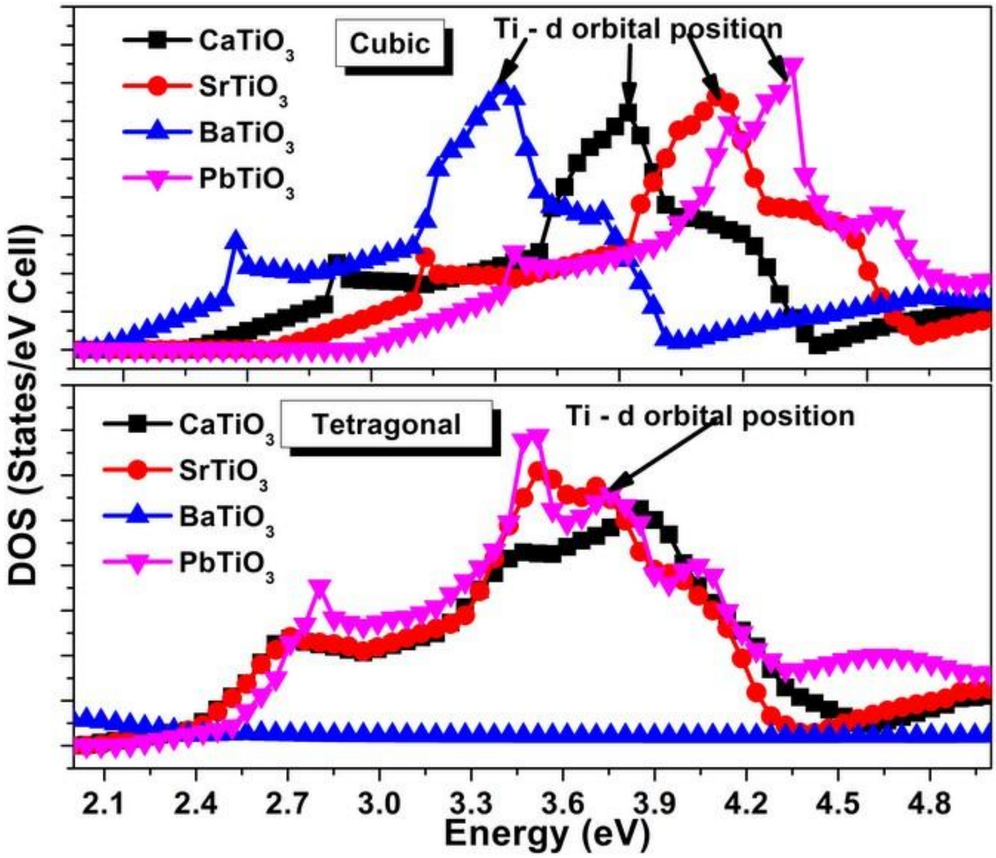

Fig.5: Ti 'D' Orbital Position in Cubic and Tetragonal Phases

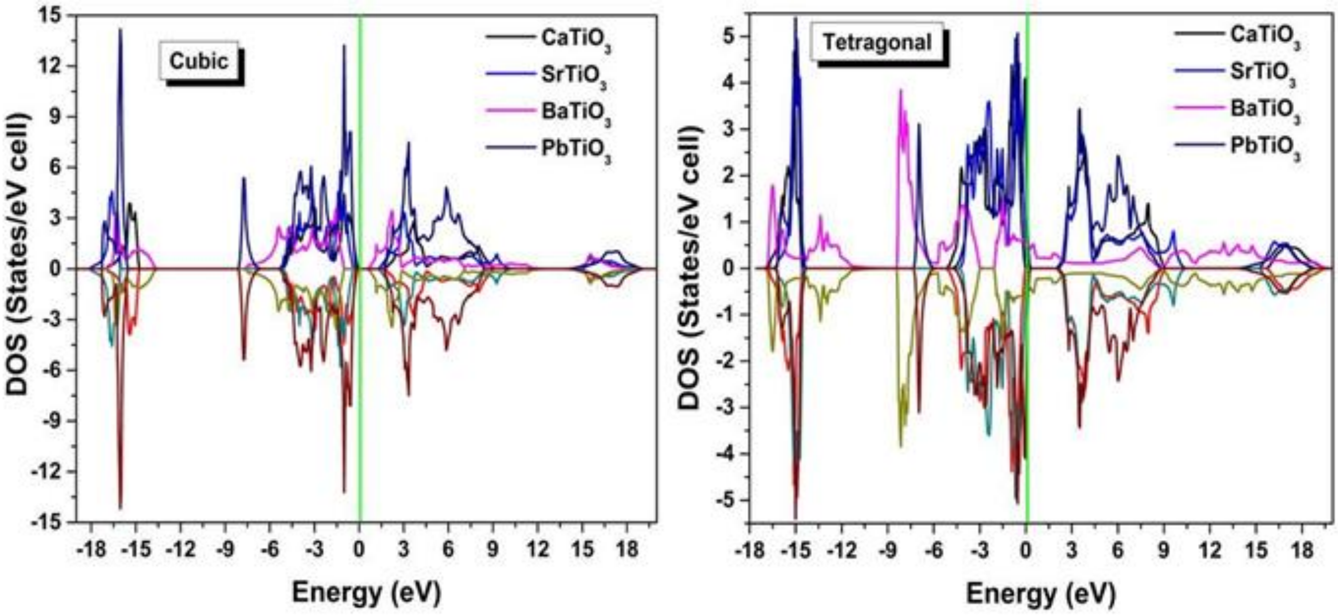

Fig.6: Electron Spins Alignment of Each Element in Atio3 Pervoskite

The spin alignments are shown in Fig.6. The presence of p-d hybridization between O and Ti gives rise to magnetization and the obtained values are confirmed with the PDOS.

Optical Properties

Refractive index and energy gap of semiconductors represent two fundamental physical aspects that characterize their optical and electronic properties. The device applications of semiconductors as electronic, optical and optoelectronic are very much determined by the nature and magnitude of these two elementary material properties. Empirical relationships modelled by a theoretical numerical analysis have been used to calculate the refractive indices of semiconductors, using their energy gaps. This physical relationship remains strictly intrinsic and specific for the material considered. The model developed stays optimized for the ternary semiconductors because they constitute an intermediate family of semiconductors. As per quantum-mechanics, the model to be developed must obey two constraints. (i) n (Eg) must have a horizontal asymptote equal to 1. (ii) n (Eg) must be hyperbolic. This means that if the band gap Eg increases, the refractive index n decreases, and vice versa, but not linearly. The equation that has been developed by Anani et al. [34] to calculate the refractive index is,

$$n = \frac{17-Eg}{5} \qquad (2)$$

Where Eg is the band gap and ‘n’ is the refractive index of the material. The calculated values of refractive indices are listed in Table 1. Exact theoretical derivations of reflection-reducing optical coatings from Maxwell equations and boundary conditions between layer and substrate have been given by Mooney [35]. For anti-reflecting (AR) coating in solar cell applications, the refractive index of the coating should be greater than that of the substrate and in fact, the difference should be as large as possible. Here all the $ATiO_3$ pervoskite compounds have higher values of refractive indices. In case of using a glass substrate, the refractive index is 1.5 whereas for $ATiO_3$ the value is above 3. From this result we infer that the $ATiO_3$ (A = Ca, Sr, Ba & Pb) compounds are the best AR materials for glass and for materials of refractive index below 2.

IV. CONCLUSIONS

Band structure, magnetic and refractive index of the $ATiO_3$ pervoskite structures were calculated and compared with cubic and tetragonal phases of each compound by TB-LMTO-ASA method. The total energy and bulk modulus of the pervoskite compounds were calculated from the Muranaghan’s equation of state and the stable phase is found to be cubic. All the compounds in cubic phase showed direct band gap whereas tetragonal phase has an indirect band gap. Valence band degeneracy was observed and it shows a semiconductor nature. A weak ionic bond exists between ‘2p’orbital of oxygen and ‘p’ orbital’s of ‘A’ cations and p-d hybridization among the O ‘2p’ and Ti ‘d’ orbital revealed the covalent bond behaviour as observed from the DOS and PDOS. This p-d hybridization has prompted us to conclude the existence of ferroelectric and ferromagnetic property in the present materials. Observed value of magnetic moments is found to be less. Both phases of $ATiO_3$ structures have higher refractive index values than glass. The results obtained suggest that they can be used for anti-reflecting coating in solar cell applications.

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