

JOURNAL OF NANOSCOPE

ISSN(P): 2707-711X Volume 1, Issue 2, December 2020, Pages: 115-124 Website: http://jn.wum.edu.pk



Pressure Induce Variations in the Lattice Constant and Energy Gap of SrThO_{3.}

Saleem Ayaz Khan^{a*}, Shahina Bibi^b, Kainat Arif^b

^aNew Technology Research Center University of West Bohemia Czech Republic. ^bDepartment of Physics, Islamia College Peshawar, KP, Pakistan.

Corresponding Email: khan@ntc.zcu.cz

Received: 30 September 2020, Published 31 December 2020

Abstract

SrThO₃ belong to stable perovskites family. Some theoretical works have been performed on this compound. However, the pressure effect in the pressure range 0 to 30 GPa was never conducted. This work highlights the importance of the hydrostatic compression on the lattice constant and energy bandgap of the compound. Lattice parameter is found to decrease with increasing pressure. SrThO₃ comes out as a direct band gap material. We discussed the effect of pressure on the energy band gap and got to know that overall energy band gap decreases as pressure increases. Finally, we discussed the density of states of SrThO₃ and plotted it against energy.

Keywords

Pressure, Lattice constant, Energy bandgap.

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1. Introduction

Perovskite oxides are the compounds with the chemical formula of ABX₃, where A and B are cations and X is an anion. This compound was first discovered by Gustav Rose in 1839 in the mountains of Russia. Its structure was first notably described by Victor Goldschmidt in 1926 [1]. Perovskite oxides are mostly of cubic structure as in BaTiO₃ but also exist in other structures such as hexagonal and tetragonal. The most common perovskite oxide compound contains oxygen as an anion but there are few perovskites that contain elements other than oxygen [2].

Perovskite oxides show many interesting and unique properties. They have properties like colossal resistance such as in (La,Sr)MnO₃ [3], fast ion conduction (Li⁺, O²⁻) batteries and fuel cells [4], mixed electronic conduction, oxidation reduction catalysts [5], ferroelectric and piezoelectric property such as in BaTiO₃ [6] and superconductivity, charge ordering [7], spin dependent transport, high thermopower [8] etc. They are used in the field of microelectronics and telecommunication [9]. They are also used in photovoltaic cells [10]. They can also generate laser light. LaAlO₃ at 1080 nm can produce laser light when it is doped with neodymium [11].

The first synthesis of $SrThO_3$ by conventional solid route was reported in 1947 by Marie-Szabo [12]. Recently Subasri *et al.*, have noted the limited thorium oxide solubility in SrO and that the formation of the pure ternary phase is not achieved [13]. On the other hand, the samples of $SrThO_3$ are prepared correctly by a sol-gel technique followed by the combustion of gel [14-16]. The properties of perovskites, such as strontium thorate $SrThO_3$, have attracted a lot of interest over the last decade [13, 14, 16]. The values of the Gibbs energy of $SrThO_3$ show that this compound is meta-stable with respect to its constituent oxide (SrO and thorium), and therefore it is difficult to eliminate the synthesis of strontium thorate. $SrThO_3$ is reported to be prepared by a conventional solid state route, Purohit *et al.*, [17] have studied the synthesis of nano-crystalline powders of $SrThO_3$ by a gel combustion route. Though there is some experimental and theoretical work on the compound, however any detailed data concerning the optical properties of $SrThO_3$ is probably not available in literature [18].

SrThO₃ was first prepared by Maric Szabo in 1947 [13]. Samples of SrThO₃ were prepared by solgel method followed by combustion of gel [16]. Benaissa *et al.*, [12] worked on the optoelectronic, elastic and thermal properties of SrThO₃. They calculated these properties using the full potential lineralized augmented plane wave (FP-LAPW) method based on the density functional theory with generalized gradient approximations GGA and low density approximations LDA. Shein *et al.*, [19, 20] discussed the elastic and electronic properties and stability of SrThO₃ using FPLAPW. Ghebouli *et al.*, [21] worked on the structural, elastic and optoelectronic properties of SrThO₃ by using the pseudo-potential plane wave (PP-PW) method. Prasad *et al.*, [16] worked on the thermodynamic studies of SrThO₃. They determined the Gibbs energy of formation of SrThO₃ using emf and monometric techniques. Ali *et al.*, [15] worked on the thermodynamic stability of solid SrThO₃. They found the Gibbs energy of formation of SrThO₃ by using the Knudsen effusion forward collection technique.

In the present wok, pressure induced physical variations in the lattice constant and energy bandgap of SrThO3 is studied. Interesting results reveals the importance of present work.

2. Computational details:

A very accurate all-electron scheme to solve these KS-equations is the full-potential linearized augmented plane wave (FP-LAPW) method as corporate in the WIEN2k code [22]. One thousand k-points are selected to integrate the Briullion zone. In the interstitial region of the unit cell the states are dealt with the plane wave like orbitals while in the muffin tin region, atomic orbitals multiplied by the spherical harmonics used to deal the core states. RKmax is selected to be seven. Suitable Rmt are chosen for the muffin tin spheres such that charge leakage from the sphere was not observed.

3. Results and discussion

3.1.Structural parameters

The unit cell of SrThO₃ consists of three atoms. The atomic positions of SrThO₃ are: Sr (0.5,0.5,0), Th(0,0.5,0.5), O(0.5,0,0.5). The study of structural parameters of a material is very important for

calculation of different properties. SrThO₃ is optimized and the structural parameters are calculated. For optimization process we selected the unit cell volume for the input from previous experimental work [12]. Then we varied the unit cell volume in the neighborhood of the experimental volume. The variation was given in three steps (+10%, 0, -10%). In the optimization process we first clicked on the x-optimize option and executed it. Then on edit optimize. Job, we uncommented "xdstart". Then we clicked on the run optimize. Job and the loop started. After completion of loop we plotted energy versus volume curve. The calculated unit cell energy and the unit cell volume $(a.u)^3$ data is fitted by using Birch-Murangan equation of state and shown in figure 1. We can see from the plot that energy decreases to particular value of volume. This particular volume is known as ground state volume and the energy is the ground state energy. Beyond this volume the energy then increases. Table 1 below gives the experimental, theoretical and present values of lattice constant, volume, bulk modulus, pressure derivative of bulk modulus and energy. From the table we can see that the lattice constant we calculated which is 4.567 Å is comparable to the other theoretical value which is 4.5503 Å [12] and to the experimental value 4.5426 Å [12]. For volume we can see that our calculated value 642.829 Å³ is comparable to the theoretical value 627.183 Å³. Our calculated value of bulk modulus which is 111 GPa is almost agreed with the theoretical value 110.5 GPa. So overall our values are in good agreement with experimental and theoretical values.



Fig. 1. Optimization plot of SrThO₃

Table 1: Shows present, expe	rimental, theoretical	values of different	parameters
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Parameters	Present work	Experimental	Theoretical
Lattice constant (Å)	4.57	4.54 ^a , 4.42 ^b , 4.43 ^c	4.49 ^e , 4.53 ^e , 4.43 ^d , 4.55 ^f
Vo	642.83		611.80 ^d , 627.18 ^e

B(GPa)	111.25	117.67 ^f , 127.59 ^e
BP	5.00	4.10 ^e , 3.65 ^f
E _o (Ry)	-59885.20	

a: Ref. [24]; b: Ref. [25]; c: Ref. [19]; d: Ref. [11]; e: Ref. [12]; f: Ref. [21];

Following is the plot of lattice constant at different pressures. We calculated lattice constants at different pressure from volume calculated from Murangan equation. The Murangan equation for volume is given as:

$$V(P) = V_{o}(1 + \frac{B_{o'}P(v)}{B_{o}})^{-1/B_{o'}}$$
Eq. 1

Where V_o is the initial volume, B_o is bulk modulus and B_o' is the derivative of bulk modulus with respect to pressure.

Here $B_0 = 109.58$ GPa, $V_0 = 642.69(a.u)^3$ and $B_0' = 5.0$

We have applied different pressures and hence different volumes are achieved. From volume we then calculated lattice constant by the following formula.

$$a = (V_{\rm o})^{\frac{1}{3}} * 0.5294706 {\rm \AA}$$

When

P = 5 GPa,	$V = 617.63(a.u)^3$ and $a = 4.506$ Å
P = 10 GPa,	$V = 596.15(a.u)^3$ and $a = 4.45$ Å
P = 15 GPa,	$V = 579.04(a.u)^3$ and $a = 4.41$ Å
P = 20 GPa,	$V = 564.52(a.u)^3$ and $a = 4.37$ Å
P = 25 GPa,	$V = 551.94(a.u)^3$ and $a = 4.34$ Å
P = 30 GPa,	$V = 540.87(a.u)^3$ and $a = 4.371$ Å

Figure 2 shows pressure versus lattice constants calculated from different values of volume at different pressures. We can see clearly from the graph that with increasing pressure the value of lattice constant decreases because as we increase pressure the atoms come closer and become compact, hence lattice constant decreases. At the start it decreases rapidly as compared to later because once the atoms become compact pressure has little effect on volume.



Fig. 2. Pressure versus lattice constant plot

3.2. Electronic properties

Solid material consists of two energy band regions. One is valence region that is the bands below the Fermi level. The charge carriers are represented with negative energy in this region. The other one is the conduction band region that lies above Fermi level. The charge carriers are represented with positive energy in this region. These bands help us to differentiate whether a material is conductor, insulator or a semiconductor. In conductor a minimum energy of 0.01eV is required for the electrons to jump from valence band to conduction band and start conduction. For insulator this energy is about 6eV which is very high because its outermost shell is completely filled. Semiconductors have band gaps below 3 eV. Semiconductors are of two types, direct bandgap and indirect band gap. In direct gap the minima of conduction band and the maxima of valence band lie at the same symmetry point in the Brillion zone and in indirect they are not.

In our present work we calculated the band structure of SrThO₃ by mBJ method. In mBJ we used five different methods to calculate band structure. We did these calculations at pressures 0 GPa, 5 GPa, 10 GPa, 15 GPa, 20 GPa, 25GPa and 30 GPa. Calculations at 0 GPa are given in the Table 2. From all these calculations we determine that SrThO₃ have direct band gap structure. Out of all of these methods the band gap calculated from original mBJ method is in good agreement with the other theoretical data [11, 24].

Following is the graph (Fig. 3-9) energy band gaps at different pressures. From overall view of the graph we can see that as the pressures increases energy band gap decreases. This is due to the decreasing bond length as the pressure is increased and unit cell volume of the compound decreased. Also the energy bandgap remains direct in the studied pressure range. In Fig. 10, direct energy bandgap versus pressure is plotted with all the methods utilized in this study as well as the experimental/available results. The results show good agreement with the original mBJ method.



Fig. 3. Electronic band structure at 0 GPa obtained from (a) original mBJ, (b) Koller *et al.*, (c) Koller *et al.* upto 7 eV, (d) Becke and Johnson and (e) Jishi *et al.* methods



Fig. 4. Electronic band structure at 5 GPa obtained from (a) original mBJ, (b) Koller *et al.*, (c) Koller *et al.* upto 7 eV, (d) Becke and Johnson and (e) Jishi *et al.* methods



Fig. 5. Electronic band structure at 10 GPa obtained from (a) original mBJ, (b) Koller *et al.*, (c) Koller *et al.* upto 7 eV, (d) Becke and Johnson and (e) Jishi *et al.* methods



Fig. 6. Electronic band structure at 15 GPa obtained from (a) original mBJ, (b) Koller *et al.*, (c) Koller *et al.* upto 7 eV, (d) Becke and Johnson and (e) Jishi *et al.* methods



Fig. 7. Electronic band structure at 20 GPa obtained from (a) original mBJ, (b) Koller *et al.*, (c) Koller *et al.* upto 7 eV, (d) Becke and Johnson and (e) Jishi *et al.* methods



Fig. 8. Electronic band structure at 25 GPa obtained from (a) original mBJ, (b) Koller *et al.*, (c) Koller *et al.* upto 7 eV, (d) Becke and Johnson and (e) Jishi *et al.* methods



Fig. 9. Electronic band structure at 30 GPa obtained from (a) original mBJ, (b) Koller et al.,





Fig. 10: Pressure versus energy band gap plot

Table 2. Band gap energy (in eV) at 0GPa

Original mBJ	Koller et al.,	Koller et al., second method	Becke and Johnson	Jishi <i>et al</i> .,	Other Theoretical values
4.23	4.41	4.88	2.81	6.29	4.23 ^a , 2.25 ^b

a: Ref. [12]

b: Ref. [24]

3.2. Density of states of SrThO₃

Fig. 11 shows the density of states of $SrThO_3$ at zero pressure. We can see from the graph that there are three energy bands. The core band lies in the range -13.38eV to -11.51eV and is mainly

occupied by Th-p orbital. The band below the Fermi level starts from -3.50eV and ends at the Fermi level. This band is mainly occupied by O-p orbital and very small contribution of Th-p and Th-f orbitals. The band above the Fermi level which is the conduction band starts from 4.59eV and it is mainly contributed by Th-f orbital and there is also contribution of Sr-d and O-p orbitals here.



Fig. 11. Density of states of SrThO₃ at zero pressure

5. Conclusions

In summary we concluded the lattice parameter, electronic band structure and density of states of cubic SrThO₃ under different pressures. Lattice parameter is found to decrease with increasing pressure. SrThO₃ comes out as a direct band gap material. We discussed the effect of pressure on the energy band gap and got to know that overall energy band gap decreases as pressure increases. Finally, we discussed the density of states of SrThO₃ and plotted it against energy.

References:

- 1. Murtaza, G. and Ahmad, I., 2011. First principal study of the structural and optoelectronic properties of cubic perovskites CsPbM₃ (M= Cl, Br, I). *Physica B: Condensed Matter*, 406(17), pp.3222-3229.
- Murtaza, G., Ahmad, I., Amin, B., Afaq, A., Maqbool, M., Maqssod, J., Khan, I. and Zahid, M., 2011. Investigation of structural and optoelectronic properties of BaThO3. *Optical Materials*, 33(3), pp.553-557.
- 3. Bason, Y., Klein, L., Yau, J.B., Hong, X. and Ahn, C.H., 2004. Giant planar Hall effect in colossal magnetoresistive La 0.84 Sr 0.16 MnO 3 thin films. *Applied physics letters*, 84(14), pp.2593-2595.
- 4. Emery, J., Bohnké, O., Fourquet, J.L., Buzaré, J.Y., Florian, P. and Massiot, D., 2001. Nuclear magnetic resonance investigation of Li+-ion dynamics in the perovskite fast-ion conductor Li3xLa2/3-x 1/3-2xTiO₃. *Journal of Physics: Condensed Matter*, *14*(3), p.523.
- 5. Su, C., Duan, X., Miao, J., Zhong, Y., Zhou, W., Wang, S. and Shao, Z., 2017. Mixed conducting perovskite materials as superior catalysts for fast aqueous-phase advanced oxidation: a mechanistic study. *ACS Catalysis*, 7(1), pp.388-397.
- 6. Wei, Y., Wang, X., Zhu, J., Wang, X. and Jia, J., 2013. Dielectric, ferroelectric, and piezoelectric properties of BiFeO3–BaTiO3 ceramics. *Journal of the American Ceramic Society*, *96*(10), pp.3163-3168.

- Retuerto, M., Emge, T., Hadermann, J., Stephens, P.W., Li, M.R., Yin, Z.P., Croft, M., Ignatov, A., Zhang, S.J., Yuan, Z. and Jin, C., 2013. Synthesis and properties of chargeordered thallium halide perovskites, CsTl+0.5Tl3+0.5X3(X= F or Cl): Theoretical precursors for superconductivity?. *Chemistry of Materials*, 25(20), pp.4071-4079.
- 8. Ullah, M., Khan, S.A., Murtaza, G., Khenata, R., Ullah, N. and Omran, S.B., 2015. Electronic, thermoelectric and magnetic properties of La₂NiMnO₆ and La₂CoMnO₆. *Journal of Magnetism and Magnetic Materials*, *377*, pp.197-203.
- Zhou, Y., Yong, Z.J., Zhang, K.C., Liu, B.M., Wang, Z.W., Hou, J.S., Fang, Y.Z., Zhou, Y., Sun, H.T. and Song, B., 2016. Ultrabroad photoluminescence and electroluminescence at new wavelengths from doped organometal halide perovskites. *The journal of physical chemistry letters*, 7(14), pp.2735-2741.
- 10. Stranks, Samuel, Snaith, Henry J. (2015-05-01) "Metal halide perovskite for photovoltaic and LED devices". Nature nanotechnology 10 (5):391-402
- 11. Deven D.J et al. (2008). "Laser action in LaAlO3". Journal of applied physics.
- 12. Cherif, Y.B., Rouaighia, M., Zaoui, A. and Boukortt, A., 2017. Optoelectronic, Elastic and Thermal Properties of Cubic Perovskite-Type SrThO₃. *Acta Physica Polonica*, *A.*, *131*(3).
- 13. I. Mary Szaba, Publ. Univ. Tech. Sci Budapest, 1, 1947, 30.
- 14. R. Subasri, C. Mallika, T. Mathews, V.S. Sastry, O.M. Sreedharan, J. Nucl. Mater., 312 (2003), p. 249
- 15. M. Ali, R. Mishra, S.R Bhardwaj et al. J. Nucl. Matter. 312 (2003) 249.
- 16. Dash, S., Singh, Z., Parida, S.C. and Venugopal, V., 2005. Thermodynamic studies on Rb₂ThO₃ (s). *Journal of alloys and compounds*, *398*(1-2), pp.219-227.
- 17. R. Prasad, S. Dash, S.C. Parida, Z. Singh, V. Venugopal, J. Nucl. Mater., 312 (2003), p. 1
- 18. R.D Purohit, A.K Tyagi, M.D Mathews S. Saha, J. Nucl matter ,280, 51 (2000).
- 19. I.R Shein and A.L Ivanoskii, Journal of structural chemistry, Vol.49, No2, pp. 348-370, 2008.
- 20. I.R Shein, K.I Shein, Ivanosvskii, J. Nucl. Matter. 361, 69 (2007).
- 21. Ghebouli, M.A., Chihi, T., Dahmane, F., Ghebouli, B., Fatmi, M., Seddik, T., Abdiche, A. and Khenata, R., 2018. Structural, elastic and optoelectronic properties of Sr-based perovskite-type oxides SrXO₃ (M= Th, Zr) via first-principles calculations. *Chinese Journal of Physics*, *56*(4), pp.1515-1524.
- 22. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, Wien2k, an Aug-mented

Plane Wave Plus Local Orbital Program for Calculating the Crystal Properties,

Technische Universit "at Wien, Austria, ISBN 3-9501031-1-2 (2001).

- 23. F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009) 226401.
- 24. M.A. Blanco, E. Francisco, V. Luafia, Comput. Phys. Commun. 158, 57 (2004).
- 25. R.L. Moreira, A. Dias, J. Phys. Chem. Solids 68, 1617 (2007).lk78ujik