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Structure simulation and study of electronic and dielectric properties of tin dioxide

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ABSTRACT

First-principles calculations based on Density Functional Theory have been done on the Tin dioxide - [SnO2]. The Orthorhombic structure of Tin dioxide has been simulated and the optimized structural parameters have been found out. Electron Density of States (EDOS) has been computed in the material using the Electronic structure calculation code of Quantum-Espresso which gives a Band gap of 1.82 eV. This value is close to the value exhibited by TCO, NLO and liquid crystalline materials. Dielectric constant of the material has been computed. The average value of dielectric constant in Tin dioxide comes out to be 8.22. Phonon modes have also been computed.

KEYWORDS

Tin dioxide;
First-principles calculation;
Electron density of states;
Band gap;
Dielectric constant;
TCO material;
Liquid crystalline material.

INTRODUCTION

Tin dioxide is a highly insoluble, thermally stable Tin source suitable for glass, optic and ceramic applications. Tin oxide is a colorless inorganic compound of tin and oxygen and found in two forms, a stable blue-black form and a metastable red form. Tin Oxide is also available in pellets, pieces, sputtering targets, tablets, films and nano-powder form[1].

Tin dioxide presents specific optical and electrical properties and has a good chemical stability. These features confer special characteristics to the SnO2 based materials. SnO2 belongs to the important class of transparent conductor oxide (TCO) materials that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum. These properties are very much essential for optoelectronic applications such as light emitting diodes, electrode materials in solar cells, flat panel displays and transparent field effect transistors[2].

Tin dioxide is also an oxidation catalyst. Its activity and selectivity can be substantially improved by incorporation of various additives. Another field in which tin dioxide plays a dominant role is in solid state gas sensors. A wide variety of oxides exhibit sensitivity towards oxidizing and reducing gases by a variation of their electrical properties, but SnO2 was one of the first Oxides that was considered for this purpose, and still is the most frequently used, material for this application. Tin dioxide can also be used as a polishing powder[3].

Tin oxide is most commonly used in glazes where it acts as an opacifier where it is typically added in the range of 5-10 percentages. When added in a specific amount, it will produce an opaque,

glossy glaze. If used in excess a dull matty glaze is obtained. Potters have used tin oxide as an opacifier for hundreds of years[4]. Its applications among others include solar energy panels, low-emission glasses and heat mirrors. Thin films of Tin dioxide have several technological applications[5, 6].

Thus study of Tin dioxide plays an important role in understanding its internal structure and to explore further novel applications of this compound. Any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material[7, 8]. Thus it is important to study the structure of the materials and look at the parameters which can be altered to get a better material for technological applications. First-principles calculation based on Density Functional Theory[9] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of materials[10, 11]. With this in view, an attempt has been made to look into the structural aspects, Electronic and Dielectric properties of Tin dioxide using the First-principles calculations.

Computational details

Several codes are available for the theoretical structure simulation[12]. The density functional theory approach has emerged as a well established computational method. It has been widely employed to arrive at the conformations of a large number of molecular systems. The practical applicability and sophistication of DFT is strongly sensitive to the good choice of exchange–correlation function along with the appropriate basis set.

Quantum espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modelling. It is based on density-functional theory, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF)[13] implementation of density functional theory (DFT), with a Local density approximation (LDA)[14] to exchange correlation energy of electrons and ultrasoft pseudopotentials[15], to represent interaction between ionic cores and valence electrons. Kohn-Sham wave functions were represented with a plane wave basis with an energy cutoff of 50 Ry and charge density cutoff of 250 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme[16] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[17] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

RESULTS AND DISCUSSION

In the present study, the orthorhombic unit cell of Tin dioxide was first built using "Avogadro"[18]. The structure was allowed for geometric optimization. Later, atomic positions of the geometrically optimized structure have been used in the plane wave self consistent field calculations.

The structure was relaxed with different values of lattice parameters. Optimized values of lattice parameters thus arrived at through minimization of energy are; 4.911Å, b=5.058Å and c=3.189Å. "scf"" calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso. Completely relaxed structure of the unit cell was visualized using the program "XcrySDen"[19] and the structure as viewed along X, Y and Z axes are given in Figures 1, 2 and 3 respectively. The bond lengths and bond angles in the relaxed structure of Tin dioxide have been tabulated in TABLES 1 and 2. Closer values of lattice parameters have been observed by Baur et. al., in tetragonal structured SnO2[20, 21].

EDOS calculation

Electron Density of States (EDOS) has been

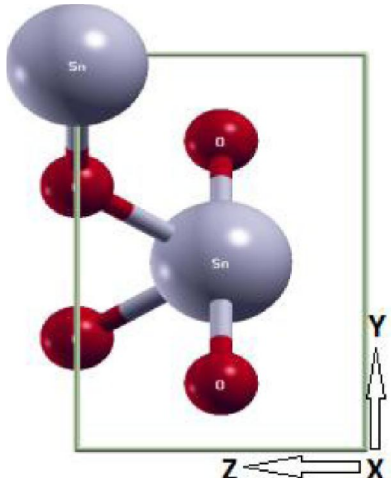

Figure 1 : Structure of unit cell as viewed along X axis

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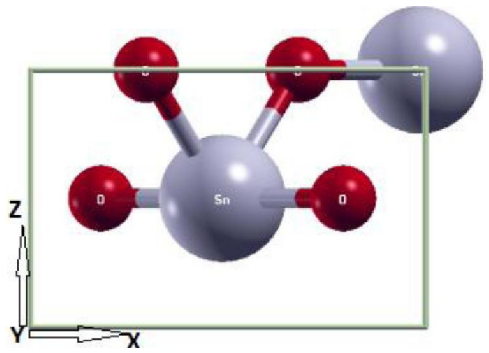

Figure 2 : Structure of unit cell as viewed along Y axis

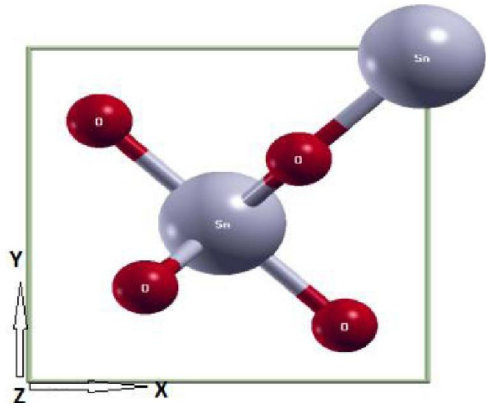

Figure 3 : Structure of unit cell as viewed along Z axis

computed using Electronic structure calculation code of Quantum espresso and is shown in Figure 4. The band gap comes out to be 1.82 eV. This value is close to the value shown by TCO, NLO and liquid crystalline materials[22-24]. Experimental measurement has shown that it has a direct band-gap with width equal to 1.814 eV. H. Salehi et. al., have found a value of 2.2 eV as the band gap in case of cubic phase of Tin dioxide[25]. A band gap of 3.6 eV has been observed in case of Rutile structured Tin dioxide[26].

Thus, nature of the properties of the SnO2 crystals depend on the structure and also on different kind of defects and impurities that are present in structure of this material. These defects could affect its structural, electronic, optical and dielectric properties.

Dielectric constant and phonon modes

Dielectric constant of the material has been computed and it comes out to be 9.87, 8.32 and 6.49 along X, Y and Z axes respectively and the average value comes out to be 8.22. Similar values of dielectric constant have been observed by Schleife et. al.,[27]. The computed phonon modes at the gamma point range from 33 cm^{-1} to 663 cm^{-1} showing that the simulated structure is stable.

TABLE 1 : Bond lengths in tin dioxide

Bond	Bond length (Å)
O – Sn	2.16
O – Sn	2.09
O – Sn	2.16
O – Sn	2.09
O – Sn	2.16

TABLE 2 : Bond angles in tin dioxide

	Bond angle (Deg)
O – Sn – O	91.1
O – Sn – O	88.8
O – Sn – O	91.2
O – Sn – O	88.8
Sn – O – Sn	130.4

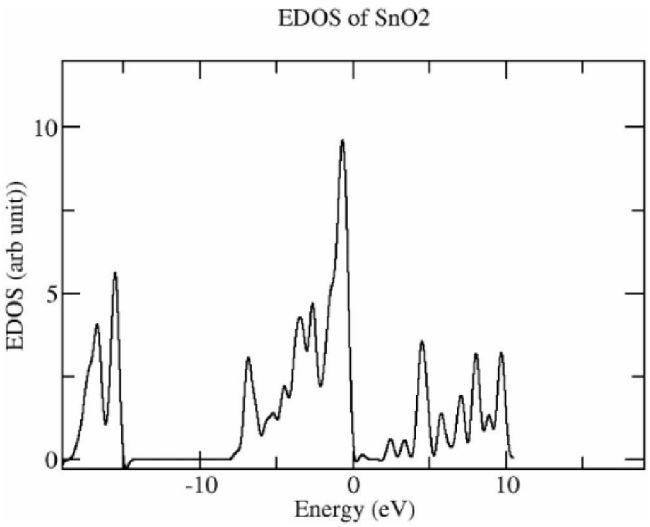

Figure 4 : Electronic density of states in tin dioxide

CONCLUSIONS

Band gap in case of Tin dioxide is found to be 1.82 eV. This value is close to the value shown by TCO, NLO and liquid crystalline materials. Hence the possibility of finding liquid crystalline nature in mixtures containing Tin oxide can be explored. The value of estimated Band gap is confirming that the material can be used for TCO applications. The average value of dielectric constant in Tin dioxide comes out to be 8.22. The computed phonon modes

at the gamma point range from 33 cm^{-1} to 663 cm^{-1} showing that the simulated structure is stable.

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REFERENCES

[1] B.Matthias, U.Diebold; The surface and materials science of tin oxide, *Progress in Surface Science,* **79**, 47-154 **(2005)**.

[2] www.inchem.org/documents/sids/sids/96311.pdf.

[3] N.Supachai, S.Thammanoon, S.Yoshikazu, Y.Susumu; Doubled layered ITO/ SnO2 conducting glass for substrate of dye-sensitized solar cells, *Solar Energy Materials and Solar Cells*, **90**, 2129 **(2006)**.

[4] A.F.Holleman, E.Wiberg; Inorganic chemistry, San Diego: *Academic Press*, ISBN 0-12-352651-5, **(2001)**.

[5] 'The Glazer's Book' – 2nd Edition, A.B.Searle, *The Technical Press Limited,* London, **(1935)**.

[6] A.K.Abass, M.T.Mohammad; Optical properties of fluorine-doped SnO2 films, *J.Appl.Phys., (United States)*, **59**, 5 **(1986)**.

[7] B.Matthias, U.Diebold; The surface and materials science of tin oxide, *Progress in Surface Science,* **79**, 47-154 **(2005)**.

[8] H.R.Sreepad, K.P.S.S.Hembram, U.V.Waghmare; *AIP Conf.Proc*. **1349**, 871-872 **(2011)**.

[9] H.R.Sreepad; *Int.J of Res in Pharmaceutical and Biomedical Sciences*, **4(3)**, 978-984 **(2013)**.

[10] M.C.Payne, M.P.Teter, D.C.Allan, T.A.Arias, J.D.Joannopoulas; *Rev.Mod.Phys.*, **64(4)**, 1045-1097 **(1992)**.

[11] H.R.Sreepad; *Int.J.Machine Intelligence*, (ISSN0975-2927), **3(3)**, 108-111 **(2011)**.

[12] H.R.Sreepad, H.R.Ravi, Khaleel Ahmed, U.V.Waghmare; *AIP Conf.Proc*., **1447(1)**, 793-794 **(2013)**.

[13] Available: http://en.wikipedia.org/wiki/Molecular_modelling.

[14] S.Baroni, Dal S.A.Corso, P.DeGironcoli, Gianozzi; Available: http://www.pwscf.org

[15] J.P.Perdew, A.Zunger; *Phys.Rev.B,* **23**, 5048-5079 **(1981)**.

[16] D.Vanderbilt; *Phys.Rev.B.*, **41**, 7892–7895 **(1990)**.

[17] H.J.Monkhorst, J.D.Pack; *Phys.Rev.B*, **13**, 5188-5192 **(1976)**.

[18] M.A.Methfessel, Paxton; (1089) *Phys.Rev.B.*, **40**, 3616 – 3621.

[19] http://avogadro.openmolecules.net/wiki/

[20] A.Kokalj; *Comp.Mater.Sci*., Available: http://www.xcrysden.org/, **28**, 155-168 **(2003)**.

[21] W.H.Baur; "Über die verfeinerung der kristallstrukturbestimmung einiger vertreter des rutiltyps: TiO_2, SnO_2, GeO_2 und MgF_2", *Acta Crystallographica,* doi:10.1107/S0365110X56001388, **9(6)**, 515–520 **(1956)**.

[22] W.H.Baur, A.A.Khan; Rutile-type compounds, IV.SiO_2, GeO_2 and a comparison with other rutile-type structures, *Acta Cryst*.B, doi 10.1107/S0567740871005466, **27**, 2133-2139 **(1971)**.

[23] D.Arivuoli; *Pramana – J.Phys*., **57(5 & 6)**, 871–883 **(2001)**.

[24] Neville Boden, Richard Bissell, Jonathan Clements, Bijan Movaghar; *Current Science*, **71(8)**, 599 – 601 **(1996)**.

[25] H.R.Sreepad; Accepted for publication in *MCLC* (Taylor and Francis), **(2015)**.

[26] Electronic and Structural properties of Tin dioxide in cubic phase.H.Salehi, M.Aryadoust, M.Farbod; Iranian Journal of Science & Technology, Transaction A, **34(A2)**, 131-138 **(2010)**.

[27] Optical properties of SnO2, Arjan Berger, Found at etsf.polytechnique, fr/sites/default/files/users/francesco/sno2.pdf, **(2010)**.

[28] A.Schleife, J.B.Varley, F.C.Fuchs, R¨odl, F.Bechstedt, P.Rinke, A.Janotti, C.G.Van de Walle; Tin dioxide from first principles: Quasiparticle electronic states and optical properties, *Physical Rev.*B., **83**, 035116 **(2011)**.