Stannates materials for solar energy applications.

by

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Abstract

Alkaline earth stannates are rare earths and are crucial material systems evident of their attractive physical properties. They are ternary metal oxide semiconductors.They have both perovskite structures ($BaSnO_3$, $SrSnO_3$) and spinel structures($ZnSnO_4$).They are compounds of tin (Sn). Broadly, these compoundsexhibit elevated melting-points, elevated thermal stability, great thermal expansion coefficient, excellent chemical resistance, small thermal conductivity and great ionic conductivity which guarantee their possible applicacability in thermal barrier coating, hosts for luminescence centers, hosts for nuclear wastes, oxygen monitoring sensors, high-temperature catalysts, solar cells applicability and solid electrolytes in large temperature fuel cells. When these materials are produced as nanoparticles, the decreased particle size as well as enlarged specific surface area could result in diverse phase transition temperatures, improved catalytic activity, and enhanced processability. Commonly, these rare earth complex oxide nanomaterialscould be fabricated via conventional solid-state reactions, coprecipitation, sol-gel, hydrothermal, self-propagation techniques, etc.In the background of energy crisis, climate change, long-term supply and security, solar energy is a striking source. For these stannates to be better utilized in solar energy harvesting applications, they are better doped.The stannates considered here are $SrSnO_3$, $BaSnO_3$ and $ZnSnO_4$.The doped stannates are used in various ways as stated above and equally as transparent conductors, light absorbers, photoanodes, etc. This is in relation to optical properties.The Optical properties, structural order and surface properties of these materials are considered. On doping, thesestannates maintain excellent transparency which makes them excellent materials as transparent conductor particularly$ZnSnO_4$. They are found highly useful in photocatalysis and other areas.In solar energy harvesting, solar energy harvesting devices could have a better output when nanostructures like doped stannates are incorporated in them. Such advance is hopeful. It improves the power conversion efficiencies (PCE) of such devices by utilizing new nanostructures to update device structural designs. This is an applauded process.

Keywords: Stannates, Barium stannate, strontium stannate, zinc stannate, doping, perovskites, spinel, solar energy, thin films, solar cells, photovoltaic.

1.0 Introduction

The amount of energy used up by humanity is greatly rising. This rise is determined by number of inhabitants' increase and advancement in human progress over the globe.The global energy demands are based on natural resources which are inadequate. These natural energy sources are difficult to arrive at. It can take about a million years to reload. However difficult, it is important to all in all works of life. But of about 7.0 billion people on earth, about 2.0 billion people live without contact with electricity, and about 2.5 billion use wood, charcoal,dung etc as major source of energy. This is chiefly used by non-advanced nations and is not a clean form of energy. It causes pollution. Fossil fuels generally cause global warming and climate change which means an increase in normal global temperatures[1].

It is obvious that global stability and sustainability will continuously be troubled by the utilization of fossil fuels. This is the trouble related to these types of energy sources. The escalation of global population, speedy technological expansion and rising energy needs will further complicate this matter. In the existing position of energy crunch and global warming, there is the necessity to build up energy production processes that protract the necessities of sustainability and renewability. There is the need for the vast upgrading in the invention and utilization of renewable energy sources for the provision of adequate energy for people and the safeguard of our immediate environment.

The adoption of the usage of a cleaner form of energy like electricity is the aim of the backward nations. However, this will mean consumption of more energy which will even be greater later as the expected world population from now to 2050 will be around 9.7 billion.

All those advanced countries shouldn't reduce their regular way of life. They should function very efficiently but should hold unto less harmful energy sources. Renewable energy sources which are environmentally harmless and tie up natural processes are many. Such are tidal power, wave power, solar energy, biomass, geothermal energy, hydroelectric energy and hot hydrogen fusion are sources that can be used to create electricity. In opposition, each of these has a major shortcoming and cannot be relied on currently for a way out to the approaching energy crunch. The main unfailing of these renewable energy sources are wind power, hydroelectric energy, biomass energy, geothermal energy, biofuel and solar energy. Amid these stated seeming unfailing renewable energy sources, solar power draws greater awareness because it is plenty, clean and without payments.

Therefore, this less harmful, renewable and serviceable energy sources which could be produced via solar energy production method requires accurate harvesting process to get high-quality sum needed by the world populace.This means that solar energy could be technically collected and utilized but there could still be an improved method of collecting the solar energy for more advanced utilization called solar energy harvesting.Achieving this energy harvesting will involve the process of doping metal oxide thin films with impurities like carbon derivatives, organic synthetic dyes etc. This will harnesses dopant characteristics for optimal performance. The doped materials help in controlling the composition and structure of dopants, which enhance their performance.

Structures of nanomaterials are different from the bulk materials. These changes made when doping them signifies some hopeful electronic characteristics, such as enhanced light absorption and speedy light response. Among all forms of nanomaterials, one dimensional materials have captivated more responsiveness in electronic device function since they are simple to produce into building blocks and simple to test with two terminals at two ends. Thus, metal oxide nanorods, nanowires, nano-needles and nanotubes are deposited by varieties of processes as they are proper for a big range of functions, like biosensors, smart windows, solar cells, supercapacitors, photodetectors, light-emitting diodes and field effect transistors.

In this book, typical consideration is given to stannates like Barium stannates ($BaSnO_3$), Srontium stannate ($SrSnO_3$) and Zinc stannate ($ZnSnO_4$) thin films deposited via solid state reactions and hydrothermal methods. However there are other numerous available methods that can be used as listed below on section for methods of synthesis. Multication oxides have more freedom to tune the materials' chemical and physical properties by altering the compositions.

Doping stannates with appropriate materials likeStibium (Sb) and Lantahnum (La), etc enhances their applications in diverse areas.

Generally, the analysis of nanoparticles traits can be done by characterization of the synthesized materials.

2.0 Solar energy harvesting

It has been proved that energy and environment are among the top list of critical troubles of people as well as civilization even in the next half of 100 years. The tremendous rise in worldwide energy utilization has amplified the exhaustion of fossil fuels. Equally, the burning of fossil fuels results to adverse environmental effects. Mutually, energy and environmental harms prompt worry on the pressing call for seeking substitute renewable and green energy. Renewable energy means any energy supply which can be replaced fast through natural procedure and practically endless, like sunshine ie solar energy, tidal power, wave power, flowing water ie hydro power, biological processes, biofuel, biomass and geothermal heat flows[2]. Up until now, these types of renewable energy have been tied together by human. Amid these stated renewable energies, solar power draws greater awareness. It is this need for solar energy as a better substitute to fossil fuel that led to fast expansion of solar industry increasing market share for photovoltaic (PV) modules which has been estimated to increase even the more between year 2000 and 2015. If solar cell of 10 % efficiency can cover 0.1% of the earth's shell, then the world power need can be supplied[3]

The figure below explains the above narration by Nobel Laureate Richard Smally.

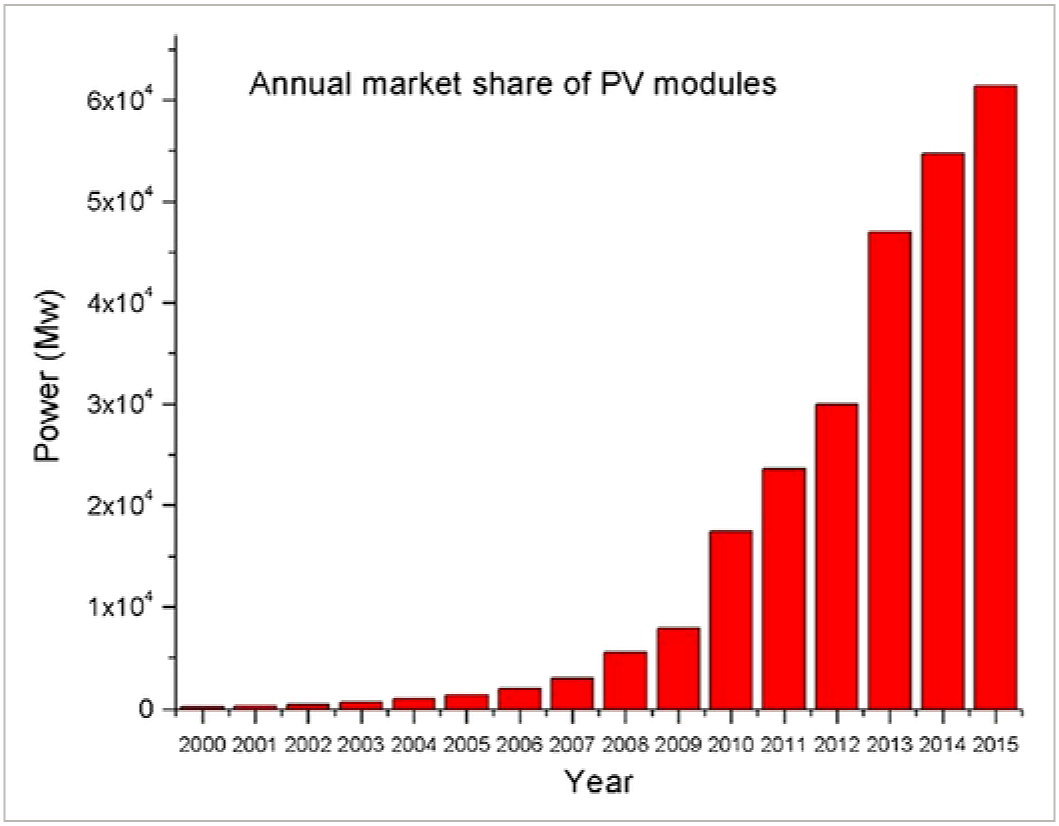


Figure 1: Increasing market share for PV modules from year 2000 to 2015

The solar energy need to be captured, harvested and utilized by processing it into useful power applications, see fig.2 below. Solar energy harvesting is the method of capturing and storing solar energy which is radiated from the sun. It will then be changed from light or heat energy to electrical energy by appropriate technique eg (a)Photovoltaic cells (Photovoltaic Modules): This is habitually said to mean solar panels and are chiefly omnipresent solar power’s harvesting technology[4].This is shown in fig. 2 below. (b). Solar thermal collectors: This can be called concentrating solar power (CSP). It is however not a well-known method of extracting solar energy.

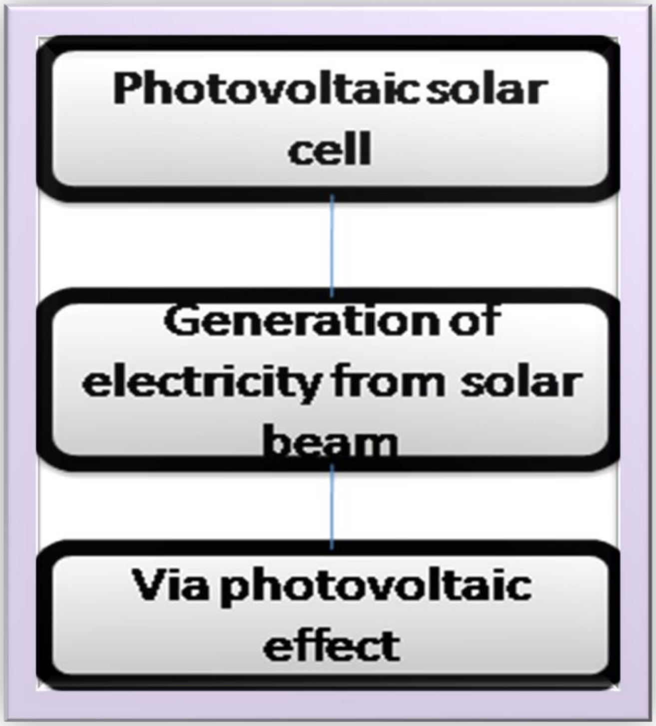


Fig.2: production of electricity using photovoltaic cells.

Solar energy harvesting could beachievedby the process of doping metal oxide thin films semiconductors with impurities like transition metal oxides, carbon derivatives, synthetic and non synthetic dyes, etc..This willpresent amazing valuable technique to achieve solar energy harvesting for improved enhancement. This process will require harnessing dopant-induced characteristics and paying attention to control of composition and structure of dopants[5].On the other hand, deposition of doped nanocrystals with specific control over composition and structure shows a considerable challenge.

Energy harvesting is helpful because it offers techniques of powering electronics when accustomed power sources are deficient. It moreover stops the requirement for changing batteries regularly and connecting wires to end applications. It is appallingly a considerable advance for valuable energy utilization. This is due to the fact that solar energy is a superior option for substituting fossil fuel as the core energy provider. It also follows thatsolar power is renewable at utterly no payments to offer energy considerably. These renewable energy sources can be used unswervingly to generate additionally other suitable types of energy. Some examples of unswerving utilization are solar ovens, geothermal heating, windmills, etc. The list of indirect exercise, that call for energy harvesting include electricity production using wind turbines, photovoltaic cells or fabrication of fuels like ethanol from biomass[6]. Some sources which could be utilized for production of electricity are; Tidal power, wave power and hot hydrogen fusion[7]. Nevertheless, every one of the above mentioned method is affected by a major shortcoming or more. This makes it unreliable as a solution to forthcoming energy crisis.

2.1 Solar energy harvestingandPhotovoltaic (PV) cells (solar cells):

Most systems, together with wireless sensor networks that harvest solar energy exploit photovoltaic (PV) cells, or solar cells, that change the energy from the sun into utilizable electricity[8]. Normally, semiconducting materials like silicon absorb photons when sunlight strikes a PV cell. The energy from the photons liberated electrons that then surge as current due to the occurrence of an electric field that has been created by the separation of charge carriers in the cell. Inserting contacts on the crest and foot of the cell allows DC current to be extracted. Solar energy harvesters exposed to direct sunlight offer the utmost comparative power density of the energy harvesting methods looked at. Nonetheless, a constraint of solar energy harvesting is that the sun will not shine throughout 24 hours in a complete day. Besides, PV cells are current sources and do not supply a stable voltage. So, even with the high power density offered, systems using PV cells need an incorporated energy storage gadget such as a rechargeable battery.

In atraditional solid state semiconductor, a solar cell is made from two doped crystals, one doped with n-type impurities (n-type semiconductor), which add additional free conduction band electrons and the other doped with p-type impurities (p-type semiconductor), which add additional electron holes. When placed in contact, some of the electrons in the n-type portion flow into the p-type to ”fill in” the missing electrons, also known as electron holes. Eventually enough electrons will flow across the boundary to equalize the Femi levels of the two materials. The p-n junction, where the charge carriers are depleted and or accumulated on each side of the surface is Seen in fig. 3 below. In silicon, this transfer of electrons produces a potential barrier of significantvoltage.

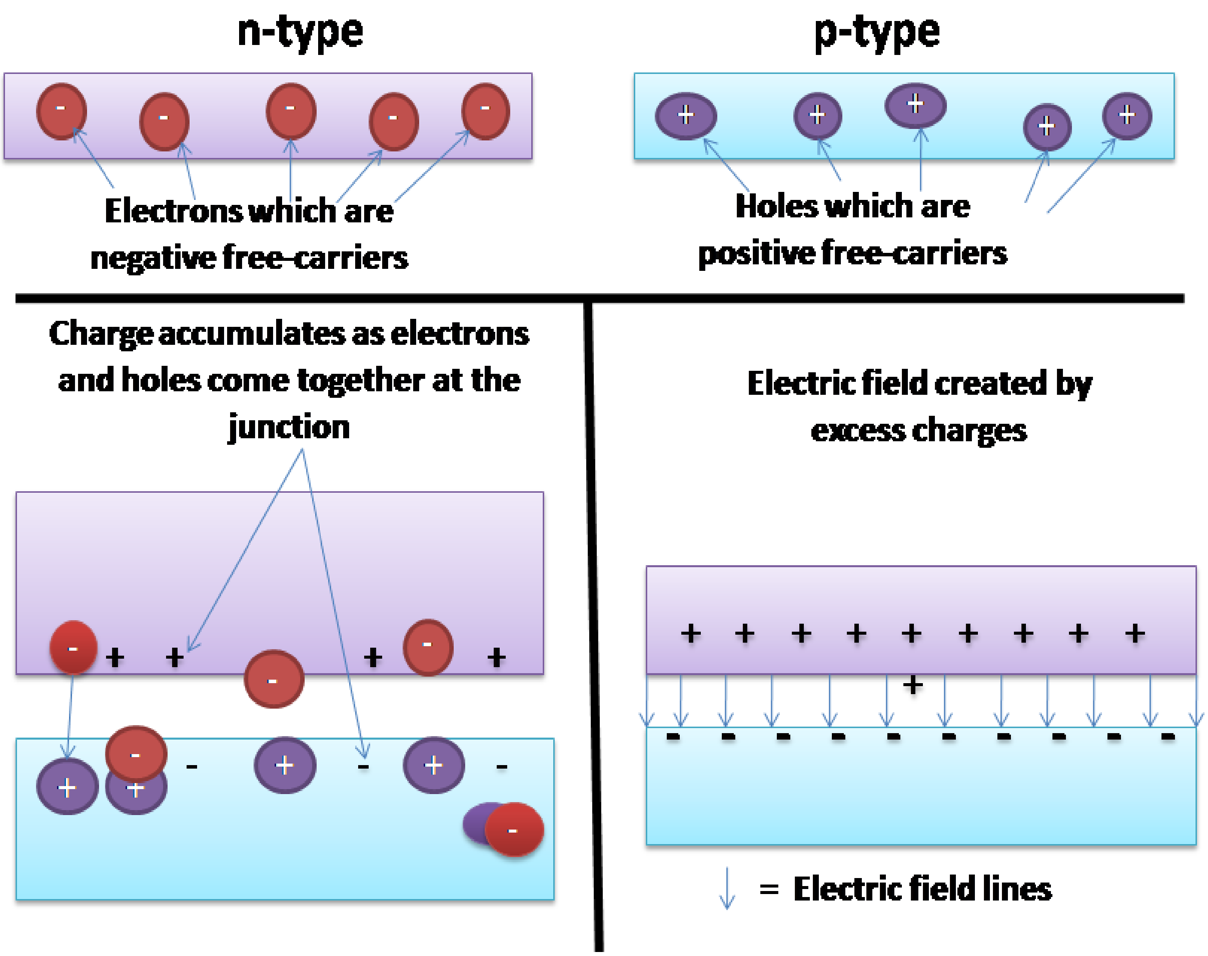


Figure 3: The p-n junction, where the charge carriers are depleted and or accumulated on each side of the surface

When placed on the sun, photons of the sunlight can excite electrons on the p-type side of the semiconductor, a process known as photoexcitation. In silicon, sunlight can provide enough energy to push an electron out of the lower energy valence band, into the higher-energy conduction-band. As the name implies, electrons in the conduction band are free to move about the silicon. When a load is placed across the cell as a whole, these electrons will flow out of the p-type side into the n-type side lose energy while moving through the external circuit and then flow back into the p-type material where they can once again recombine with the valence band hole they left behind. In this way, sunlight creates an electric current.

In any semiconductor, the band gap means that only photons with that amount of energy, or more, will contribute to producing a current. In the case of silicon, the majority of visible light from red to violet has sufficient energy to make this happen. Unfortunately, higher energy photons, those at the blueand violet end of the spectrum, have more than enough energy to cross the bandgap though some of this extra energy is transferred into the electrons, the majority of it is wasted as heat. Another issue is that in order to have a reasonable chance of capturing a photon, the n-type layer has to be fairly thick. This also increases the chance that a freshly ejected electron will meet up with a previously created hole in the material before reaching the p-n junction. These effects produce an upper limit on the efficiency of silicon solar cells, currently around 12 to 15% for common modules and up to 25% for the best laboratory cells. (33.16 %) is the theoretical maximum efficiency for single bandgap solar cells.

By far, the biggest problem with the conventional approach is cost; solar cells require a relatively thick layer of doped silicon in order to have reasonable photon capture rates, and silicon processing is expensive. There have been a number of different approaches to reduce this cost over the last decade, notably the thin film approaches, but to date they have been limited application due to variety of practical problems. Another line of research has been to dramatically improve efficiency through the multifunction approach, although these cells have very high cost and suitable only for large commercial deployments.

3.0 Current technology

stannate perovskite oxides have equally attracted a great deal of interest because of their possible use in the area of solar energy. When a stannate material is illuminated with light, charge carriers (electron-hole pairs) are generated. These photo-generated carriers are seperated and driven to the electrodes by the polarization induced internal electric field, causing a photovoltaic output. The photovoltaic effect in stannate is a bulk-based effect, which differs from the junction based semiconductor photovoltaic effect. Since the internal electrc field is not limited to an interfacial region in a stannates, photovoltaic response can be generated without forming complex junction structures.

The solar cell, otherwise called photovoltaic (PV) cell was developed to change sunlight to electricity via PV effect procedures. In any case, its business in home utilization is restricted due to the expensive and complicated production technique for a usual silicon-based solar cell. It is the bid to cut down this high cost and at the same time retains the efficiency that brought about the production of DSSCs which is a third generation solar cell and other types of solar cells. The 15 % or more efficiency achieved by DSSC was when perovskite was used as sensitizer. Other novel techniques have also got the attention of scholars.

3.1 Types of solar cells:

3.1.1 Semiconductor solar cells:

In semiconductor materials, the majority charge carriers are electrons and the Femi levels lies closer to the conduction band of the semiconductor. A variety of such materials such as TiO_2 (Nowotny et al. 2008; Park et al. 2000; Barbe' et al. 1997; Wong et ai. 2006) ZnO, Fe_2O_3, Nb_2O_5,CeO_2, Zn2SnO4,$SrTiO_3$ and $BaSnO_3$, have been tested as photoanodes in DSCs/DSSCs.

In a traditional solid state semiconductor, a solar cell is made from two doped crystals, one doped with n-type impurities (n-type semiconductor), which add additional free conduction band electrons and the other doped with p-type impurities (p-type semiconductor), which add additional electron holes. When placed in contact, some of the electrons in the n-type portion flow into the p-type to ”fill in” the missing electrons, also known as electron holes. Eventually enough electrons will flow across the boundary to equalize the Femi levels of the two materials. The p-n junction, where the charge carriers are depleted and or accumulated on each side of the surface. See fig. 3 below. In silicon, this transfer of electrons produces a potential barrier of about 0.6 to 0.7 V.

3.1.2 Dye sensitized solar cells:

This is a third generation solar cell. Its history was dated back to 1972 when ZnO (zinc-oxide) photo-anode sensitized with chlorophyll was used. It was discovered that the cell effectiveness was small because of inadequate surface area available for light harvesting. It was in 1991 that nanostrctured titanium dioxide (TiO_2) film was covered with a monolayer of ruthenium dye as photoanode and was achieving self-efficiency of 7.1-7.9 %. The nanostructured TiO_2 film extensivelyimproved the obtainablesurface area by a factor greater than a thousand, which was necessary for competent dye loading. This advanceenhanced the light absorption and efficiency of DSSC considerablywhich made DSSC to be looked at as a strong competitor to their obtainable solar cell know-how. From there, the efficiency and stability of DSSC have continuously improved out of research. Nazeerudeen et al reported DSSCefficiency of 10.4 %, Chiba et al reported that of 11.1%, Mathew et al reported 13 % while 15 % obtained is based on perovskite sensitizer. To get a high-efficiency DSSC, it is imperative to comprehend the kinetics of photoexcited electrons in the photoelectrochemical cell throughout its operation. It is important to know the performance of photo-excited electrons in DSSC. The photo-anode plays a significant role in governing the collection and transportation of photoexcited electrons. The variations of photo-anode in terms of morphology, doping and film thickness have importantcontrol in the PV performance of DSSC.

3.1.3perovskite solar cells (PSCs):

Perovskite solar cells based on organometal halides represent an emerging photovoltaic technology. Perovskite solar cells stem from dye-sensitized solar cells(DSSCs).

When perovskite sensitizer was used in DSSC, an efficiency of 15 % and even more was achieved[9].

The hybrid organic-inorganic metal halide perovskite gives about the best solar cell operation like methylammonium lead iodide ($CH_3NH_3PbI_3$) or methylammonium lead bromide ($CH_3NH_3PbI_3$). The advancementin perovskite solar cells shifted from methylammonium lead halide ($CH_3NH_3PbX_3$) (X=Br, I) sensitized liquid solar cell at 3.8 % to over 20 % of formamidinium lead iodide iodide ($NH_2CHNH_2PbI_3$) solar cells from 2009 to 2015[10]. Qin et al. (2014) offered an apparatus configuration comprising of titanium dioxide as a scaffold as well as electron collector, lead halide perovskite as the light harvester and CuSCN as the hold transport material (HTM) with high power conversion efficiency of about 12.4 % under full sun illumination.

3.1.4 Spinel oxide solar cells

Numerous spinel oxides of AB_2O_4 formare seen as light absorbers for all-oxide thin film photovoltaic cells due to their almost perfect optical band gap of about 1.5 eV, that can get to 40% of the theoretical conversion efficiency.Some spinel oxides were seen as alternative materials for photoanodes in thin film photovoltaic cells due to their wide optical band gap of about 3.6 eV.

Equally, there is the heterojunctions of spinel oxides for inorganic solar cells like TiO_2/Co_3O_4 where Co_3O_4 is a p-type semiconductor, which has two noticeable direct transitions in the visible range with band gaps energy of about 1.45 eV and 2.26 eV.

All-oxide photovoltaics could be the next generation of photovoltaic cell.

3.2 Crystal structures of spinels and perovskites stannates:

3.2.1Crystal structures :--Spinel

Here we consider zinc stannate spinel structurebelonging to space group$Pm\overline{3}m$. The spinel structure is formulated as$MM^1{}_2X_4$, where M and M^1 are tetrahedral and octahedral. The structure is named after the mineral $MgAlO_4$. The compounds from this family can be represented by a different general formularAB_2O_4. Where A and B are either divalent (+2) and trivalent (+3) or tetravalent (+4) and divalent cations. The crystal structure could be determined independently[11].

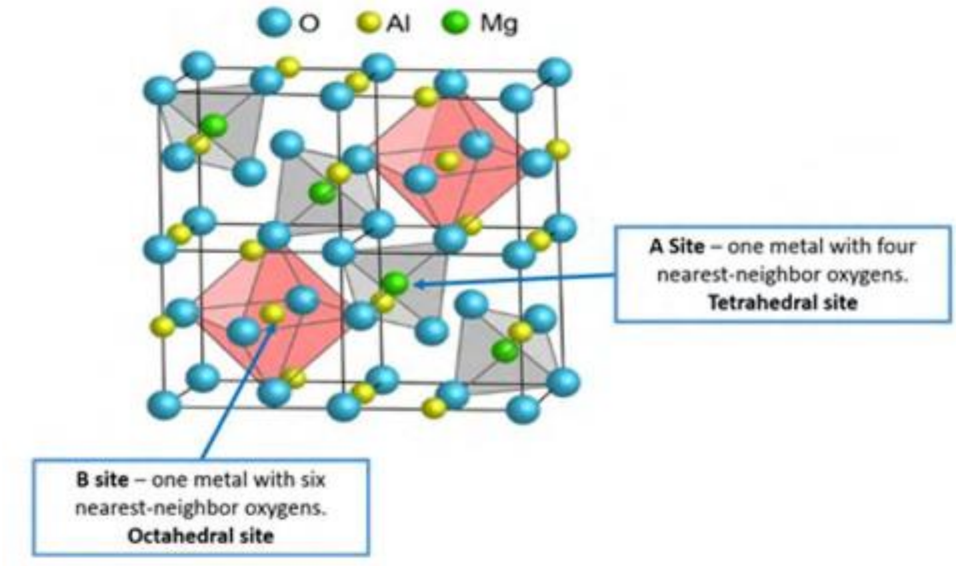
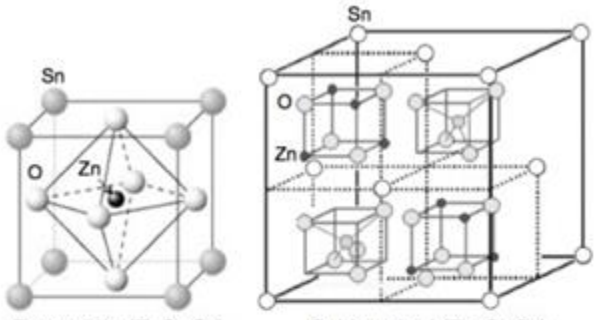


Figure 4: Schematic of the spinel structure of $MgAl_2O4$



Perovskite $(ZnSnO_3)$ Cubic spinel (Zn_2SnO_4)

Figure 5: Crystal structures of zinc stannate: perovskite structure for zinc metastannate, $(ZnSnO_3)$ and cubic spinnel structure of zinc orthostannate$(ZnSnO_4)$. A single atom of each element is labeled in the structural diagrams.

Cubic spinels have been assigned to the space group $Fd\bar{3}m.$ the unit cell of a spinel consists of eight formular units with the oxygen ions forming a closed-packed face centred structure.

3.2.2 Crystal structure—perovskite:

A perovskite is any substance with a crystal structure like that of a mineral known as perovskite. This has calcium titanate oxide$(CaTiO3)$ structure. The perfect cubic structure has the B cation in 6-folds coordination surrounded by an octahedron of anions and the A cations in 12 folds cuboctahedral coordination[12].

The perovskite structure has simple cubic symmetry, but is related to the fcc lattice in the sense that the A site cations and the three O atoms comprise a fcc lattice. The B-site cations fill ¼ of the octahedral holes and are surrounded by six oxides anions.

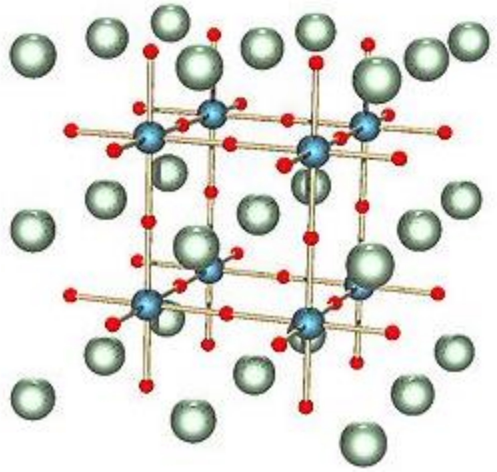


Fig 6: ABX_3 perovskite structure. Here, A, B, and X are white, blue, and red, respectively.

3.3 Band structure

The conduction band structure of cubic $SrSnO_3$ is qualitatively related to that of $BaSnO_3$.

The optoelectronic properties of spinel oxides are directly related to their band structures, as most of transition metal oxides. In general the valence band (VB) is filled with oxygen orbitals (orbitals $2p^6$-full) while the conduction band (CB) consists of cations orbitals (orbital d-empty). Depending on the value of the band gap, the oxide presents a semiconducting or insulating behavior. The simplified and general band structure diagram of transition metal oxides is shown in fig. 7below.

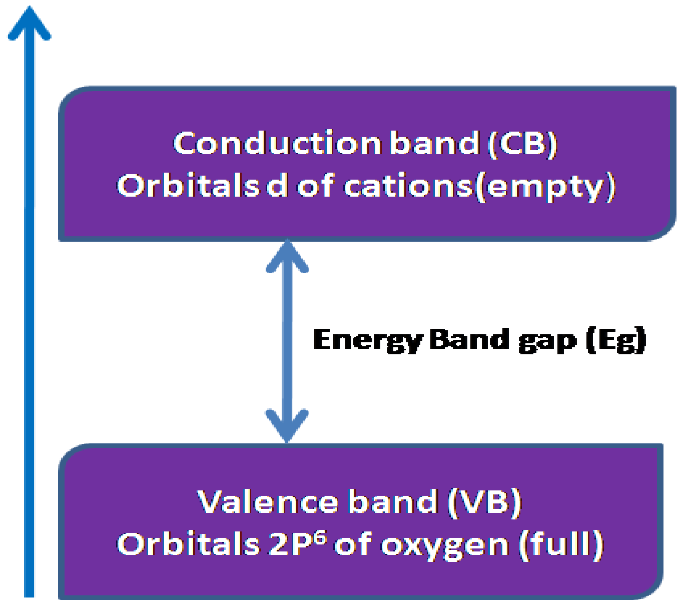


Fig.7Thecommon diagram of transition metal oxide band structure

The light absorption characteristics of spinel oxides are associated to the charge (electron) transfer in material. There are two key groups of electronic transfers:

In spinel type oxides, the charge transfers of cation-oxygen (band theory) gives the highest absorption intensities. When the energy band gap value of an oxide compound is in the visible range, the absorption phenomenon is explained by a transfer of electrons from the orbitals $2p^6$ of oxygen (VB) to the empty orbitals $3d^1$ of metal cation (CB).

Some transition metal oxide with wide band gap may appearand transparent whilesome with wide band gap appear coloured when doped with an electron acceptor element or electron donor elementin the form of impurities. Other absorber properties of transition metal oxides are related to interatomic charge transfer between cations, which is called an intervalence charge transfer, representing an internal oxidation-reduction process. Such transfer may be direct (in the case of orbital overlap cations) or indirect (via transfer oxygen). It occurs between two different oxidation states of cations[13].

4.0 Doped stannates.

Doping is the deliberate addition of impurities into a material to be able to manage the qualities of the materials. It improves the uniqueness of the material doped eg metal oxide nanoparticles/thin films and enhances its appropriateness for diverse fields. Doping nanomaterials gives a stretchy way to change the qualities of the materials whilst keeping their high surface areas. It is an extensively utilized method for the alteration of nanoparticles to boost their electrical, optical and biological activities. It has been evidenced that doping may enhance the antimicrobial effect

It actually depends on the class of nanomaterial that will comprise the medium. The doping process will vary in case of metallic nanoparticles, oxides or semiconductor (e. g. chalcogenides). Nevertheless, the common trend is to add the doping precursor at the beginning of deposition, before the nucleation of NPs, in the preferred molar ratio and a yield of about 100% is predicted. For metals, the precursors are normally metal salts.For oxides it might be an alcoxide, an organometallic compound or a complex of the transition metal like acetylacetonate. The mechanism of nucleation+ growth for the material is a decrease method (like for metal NPs), a sol-gel process (for oxides) or a thermal decomposition (for some chalcogenides)[14].

Doping diverse elements helps to change and direct the material towards required relaxation properties like electronic, optical, photochemical, photoelectrochemical, photocatalytic and photoexcited properties. The substances can be engineered towards particular usages by cautious choosing of the dopants. Doped nanoparticles, gives the anticipation that doped materials will find applications in optical storage, radiation detection, infrared detection, and dosimetry[15].

The energy structure and physical characteristics of doped nanomaterials plus nanodevices are being affected by quantum size confinement. Near-infrared and up conversion luminescence nanoparticles are particularly hopeful for biological imaging because auto-fluorescence can be overcome and higher imaging resolutions can be obtained. Doped insulator nanomaterials as well as carbon nanotubes signify a new dimension. As a novel kind of biological labeling agent, insulator nanoparticles are less poisonous than semiconductor nanoparticles and are skilled for cancer detection, diagnosis, and treatment. Doped nanomaterials are likely to make central assistance to nanotechnology for practical usages in the fields of electronics, photonics, optics, homeland security, and medical sciences.

Doping of metal oxide thin film semiconductors with transition metals presents amazingly valuable technique to achieve solar energy harvesting for improved enhancement. Doped oxide nanocrystals embrace pledge for a broad range of use if dopant-induced characteristics properties can be suitably harnessed. On the other hand, deposition of doped nanocrystals with specific control over composition and structure shows a considerable challenge. Nanocrystal composition is difficult to manage owing to the contrary reactivity of dopant and host precursors. The multiplicity of dopant atoms which could be included is restricted, with effectiveness of dopant atom inclusion varying. [16]

Moreover, the enlarged electron density resulting from the doped resources enhances the fill factor of the solar cell. The enlarged electron density speeds up the transfer rate of electrons in the doped resources of metal oxide thin films when in contrast with undoped films. This could be established using intensity-modulated photocurrent spectroscopy measurements.

The above analogies are applicable to dopped stannates.

Stibium (Sb), Lantahnum (La) etc can be used to dope stannateslike $BaSnO_3$ (BSO) to a highly conductive status. When doped with La, it is called Barium Lantahnum Stannic Oxide (BLSO) which has tremendous metallic conduction

5.0 peculiarities/properties of the stannates

The term stannatemeans compounds of tin (Sn).They are ternary metal oxide semiconductor The stannates under consideration in this chapter are: Barium stannate (Ba_3SnO), Strontium stannate ($SrSnO_3$) and Zinc stannate ($ZnSnO_4$). The $BaSnO_3$ and $SrSnO_3$ have perovskite structures while ZnSnO4 has spinel structure. The common formular for the stannate based perovskite type is $ASnO_3$ while that for spinneltype is $ASnO_4$[17].

Alkaline-earth metal is any of the six chemical elements that comprise Group 2 (IIa) of the periodic table. The elements are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). Zinc stannate (ZSO) which is of spinel nature equally belongs to alkaline-earth stannate class like the perovskite natured stannates. It is not a perovskite type but can be an alternative to perovskite substance. It has a non-cubic structure and belongs to R3c space class. Its lattice constant is α=7.758 Å. Barium stannate (BSO)isamong the $Pm\overline{3}m$ space group. It has α=4.139 Å as its lattice constant. Equally, strontium stannate (SSO) is a member of the Pbnm space class. It has average size of 45 nm. It has lattice constant α=5.709 Å which is pseudocubic.

The alkali earth stannates ($MSnO_3$or $ABO_3$where M or A=Sr, Ba, etc) are distinctive for their good stability at high temperatures and outstanding dielectric and sensing properties and are widely used in capacitors, moisture sensing, solar cells, etc.
The term stannate is also used in naming conventions as a suffix for example the hexachlorostannate ion is $SnCl^{2-}_6$.

One of the mainset of substancesbelongs to the set of alkaline earthstannate where the A siteis to be occupied by either Ba or Sr with the ionic radius of 135 pm and118pm. Even thoughthey have wide optical band gaps, the electron conductivity is outstandingly better. In electronic industries,they are equally largely applied. This is as a result of their unbelievable dielectric and gas sensing characteristics. Alkaline earth stannates are equally applied in conductive resulting to drawing attention to great noticein technology. In production of transparent electrodes involving utilization in photovoltaic cells and organic light-emitting diodes, stannates play a wonderful role.Stannates are equally used in sensor advancement.

Transparent conductors are materials that have DC electrical conductivity but transparent to light over a wavelength range of interest making them essential in solar photovoltaics, displays and other technologies.

The phase purity, crystallization idiosyncrasies and microstructural evolution and etc of derived alkaline earth metal stannate powders could be studied by XRD and SEM measurements and etc.

The photovoltaic performance of $SrSnO_3$ nanoparticles is used as electrode material in DSSCs.

Substances that have perovskite structure have shown excessive fascinating physical characteristics, like, great photovoltaic effects, superconductivity etc.

5.1 Barium Stannate(Barium Stannic oxide), (Barium Tin Oxide),$BaSnO_3$(or BSO)

The Barium Stannate is an n-type substance which has cubic perovskite structure with band gap of about 3.4 eV. It maintains stability even at 1000^0C[18]. It is among the $Pm\overline{3}m$ space group. It has α=4.139 Å as its lattice constant. Its applications are numerous, they are used as: thermally stable capacitors, humidity sensors, gas sensors, etc. it is also used in optical applications, capacitors, ceramic boundary layers, and equally a promising material to produce gas phase sensors for the detection of carbon monoxide and carbon dioxide[19].

The figure below shows the cubic configuration of Barium stannate of $Pm\overline{3}m$ class.

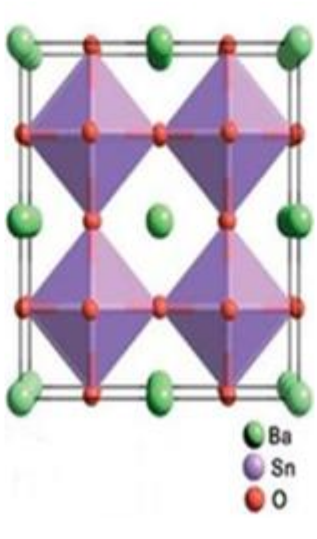


Figure 8:Cubic configuration of Barium stannate of $Pm\overline{3}m$ class.

Stibium (Sb) and Lantahnum (La)and other dopants can be used to dope BSO to a highly conductive status. When doped with La, it is called Barium Lantahnum Stannic Oxide(BLSO) which has tremendous metallic conduction as depicted in table 1 below.

Apart from working better due to high mobility, BLSOequally has good stable state for sustenance at elevated thermal conduction[20]. However, BSO in its epitaxial form has lesser mobility, which actually is contradicting to the very high mobility of BSLO. This is as a result of grain boundaries and dislocation that is causing charge traps and scattering and consequently bringing down the carrier density and mobility at the same time.

When lattice-matched substrate is selected, it will help to lessen dislocation as well as grain boundaries thereby improving dislocation in thin films[21].

Table 1 The BSO Performance

Dopant	Bandgap (eV)	Resistivity (Ω/cm)	Conductivity (S/cm)	Mobility ($cm^2V^{-1}s^{-1}$)	Trans (%)	Deposition method
Lantahum	4.05	$5.9x10^{-4}$	1695	103	-	Solid state reaction
Lantahum	-	$10\ x10^{-3}$	100	320	-	” (single crystal)
Lantahum	-	-	-	70	-	Pulse layer depositn (epitaxial films)
Lantahum	-	-	-	150	-	Modified MBE
Lantahum	3.95	-	-	-	>80	Sol-gel

Barium stannate, when prepared by solid state reaction, served as starting material for further heat treatment. Suitablequantities of $BaCO_3$ as well as dried SnO_2mutually of purity greater than 99.5 % were homogenized in agate motor for 6 hrs as the mixing medium. The homogenous mixture that was got was heated in an alumina crucible up to temperature 1000 ^{0}C. It was maintained at a temperature of about 8 hrs. There was addition of polyvinyl alcohol into the powder which was calcined for the synthesis of pellets. This was burnt out via elevated temperature sintering. Weight of quantity 5 tonutilized for the synthesis of pellets of circular disc shape. The pellets were grinded and sintered in a platinum crucible up to a very high temperature of about 1250 ^{0}C for six hours

The structural, morphological and optical properties of the materials could be examined extensively. The crystalline quality and crystallographic orientation could be studied by X-ray diffraction analysis using wavelengthof 1.54060 Å in 2θ range of 10-100 ^{0}. The vibrational spectrum could be carried out using micro-Raman spectrometer applying a laserradiation ofwavelength 514 nm from an argon ion laser. The spectrum could be carried out usingspectral resolution of 1 cm^{-1}. The morphology and elemental analysis of the compound could be studied using Energy Dispersive X-ray spectrometer. Both absorbance and reflectance spectra of the material in the spectral range of 200-900 nm could be carried out using UV-visible double beam spectrometer. The TEM of the image could be studied using electron microscope working at 200 KeV.

The XRD pattern of $BaSnO_3$powder was prepared by solid state reaction method and it presents a polycrystalline nature. X-ray diffraction pattern of the prepared sample presents all the characteristic peaks of cubic phase of $BaSnO_3$. The inter planar distance 'd' of the powder is calculated using Bragg's relation $2d\sin\theta=n\lambda$ where λ is the wavelength of the X-ray radiation and $\theta$is the diffraction angle. The lattice constant for the compound was calculated and found to be 4.101 Å which is in agreement with the reported value (4.112Å)[1].The avarage crystallite size $D_{(hkl)}$ of the powdercan becalculated using theDebye Scherrer's formular.

$$D_{(hkl)}=\frac{K\lambda}{\beta cos\theta} \text{ --(eqn 1)}$$

The average size of the crystallites was found to be 49 nm. This shows the nanocrystalline nature of the powder.

The micro-Raman spectrum of the Barium stannate powder prepared in the present case by solid state reaction method presents a very intense band at 1054, intense band at 560,139 and weak intense band at 686,336,1130. The 1054 is due to $BaCO_3$. The Raman bands found to be~ 139, 833, and 1130 cm^{-1} can be assigned on the basis of fundamental vibrations of SnO_6 octahedron which has O_h symmetry, in the distorted perovskite structure.

The figure below depicts the SEM image of $BaSnO_3$ andalsoshown below depicts a porous surface morphology containing grains of cuboidal structure having fine definite grain boundaries. The elemental studyof the compound using EDS analysis maintains the formation of the compound.

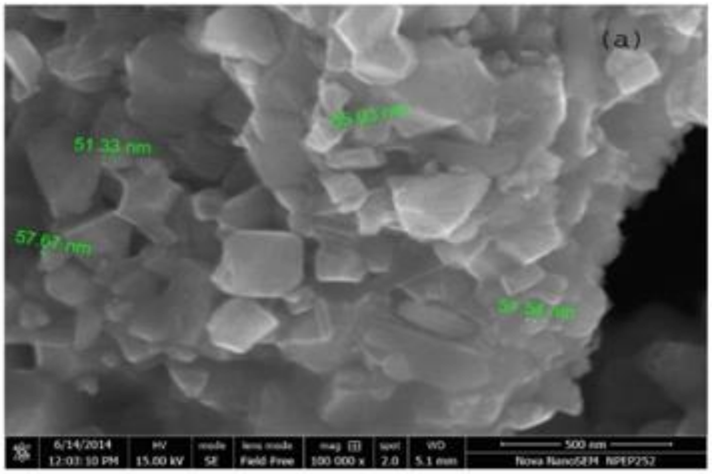
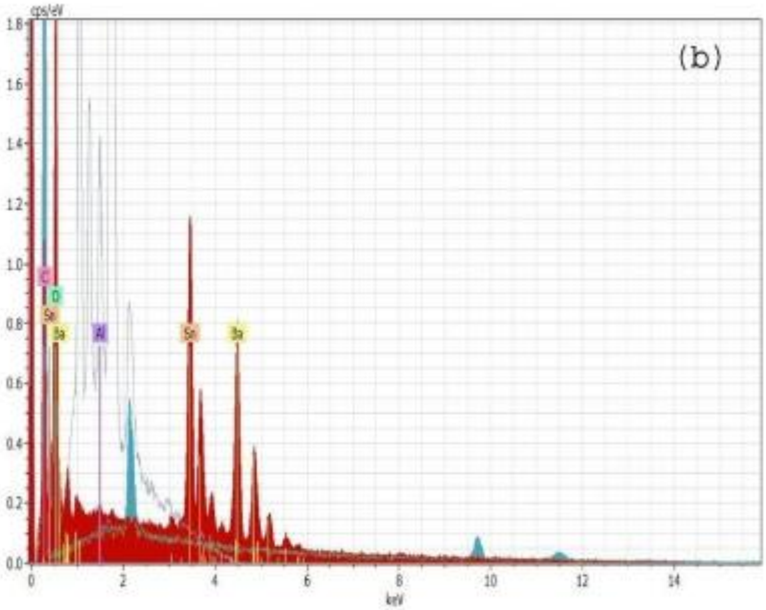


Figure 9: The SEM images of $BaSnO_3$ fabricated via the process of solid state reaction.

Equally, the figure 8 below depicts the EDS spectral analysis of the barium stannate powder fabricated via solid state route. The EDS spectra shows indication of the deposition and formation of compound.



Figur 10: The EDS images of barium stannate deposited via solid state reaction routes

The figure 11below is a TEM imageinvestigation showing a high resolution of nanostructural and morphologicalcharacterization of barium stannate powder. It has particle size of 55 nm which could be calculated from using TEM analysis. This finding corresponds with XRD and SEM analysis. The porousity of the surface morphology having grains of cuboidal structure is also depicted by TEM image.

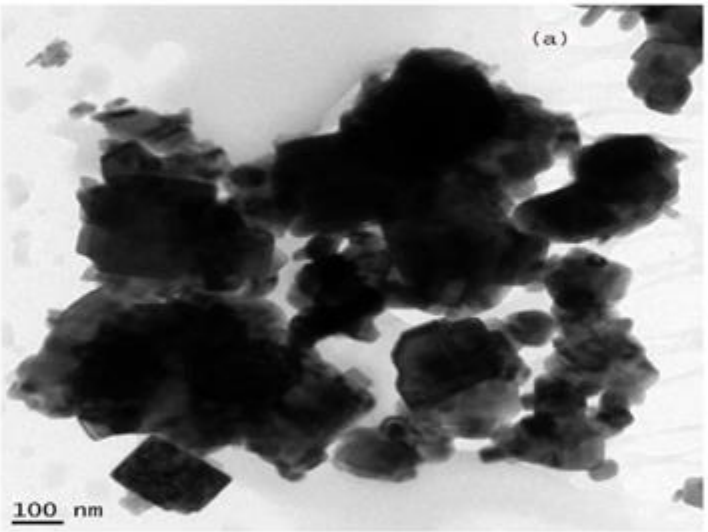


Fig 11: TEM image of barium stannate synthesized via solid state reaction route.

5.2 Strontium stannate, (Strontium Stannic oxide), (strontium tin oxide), $SrSnO_3$ (SSO)

Strontium stannic oxide ($SrSnO_3$)is an n-type material and a perovskite with orthorhombic structure as shown in figure 11 below. It is a member of the Pbnm space class. It has average size of 45 nm[22]. It has lattice constant α=5.709 Å which is pseudocubic. It has b=5.703Å and c=8.065 Å. Its energy band gap is large, about 4.27 eV.The band gap transition is indirect (m=2). Band gap energy of semiconductor nanoparticles increases with a decrease in the grain size.

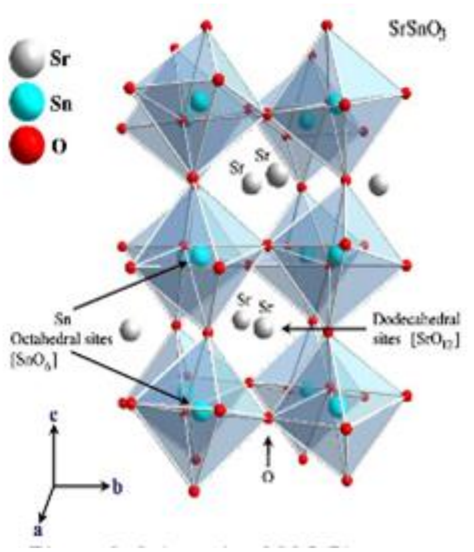


Fig. 12: Orthorhombic arrangement of SSO of Pbnm group.

It is synthesized using solid state reaction, chemical bath, simple wet chemical reaction, electrochemical methods etc. In our work, solid state reaction technique is considered.

Commonly, $SrSnO_3$ powders (for industrial application) is synthesized using solid state reaction. This technique is simple and cheap. Strontium carbonate and titanium dioxde or strontium carbonate ($SrCO_3$) and tin oxide (SnO_2) which are of high purity, up to 99 % are used as starting marterials. Over 900 ^{0}C calcination temperature and a long time is needed in this method. This however has many disadvantages including big particle size with big size distribution and big degree of particle agglomeration. When they are mixed stoichiometrically by ball milling with zirconia media in ethanol for 24 h and later calcined at 1100 ^{0}C after drying for 6 h in air, theprocess produces a uniform, facile, small sized $SrSnO_3$ powder. The starting materials could be:strontium carbonate ($SrCO_3$) and tin oxide (SnO_2) which are of high purity, up to 99 % as stated above.

The $SrSnO_3$could be doped with impurity such as La, Ne, etc. As doping increases, the distortion in the orthorhombic pattern 0f the perovskite configuration in SSO results to absorption in the visible. Smaller lattice parameters are betterwell-matched with ordinary oxide electronic substrates. The mobility performance of SSO is lower than that of BSO perovskite. Liu et al. were able to get a mobility of 18.5 $cm^2V^{-1}s^{-1}$ when they introduced Tantalum (Ta) as dopant.

This can be seen in table 2 below. The potential barrier is reduced when the carrier concentration and ionization efficiency become higher as a result of raising the Ta content. Due to that, mobility is tremendously enhanced by half a 100 folds compared with the previous achievements.

Table 2: SSO performance

Dopant	Bandgap (eV)	Resistivity (Ω/cm)	Conductivity (S/cm)	Mobility ($cm^2V^{-1}s^{-1}$)	Trans (%)	Synthesis method
Erbium	-	$0/1x10^{-3}$	$1x10^{6}$	-	-	Sol-gel
Stibium	4.53	$23x10^{-3}$	43.48	0.329	>90	Pulsed laser deposition
Neodymium	-	$21x10^{-3}$	47.62	0.104	>90	Pulsed laser deposition
Tantalum	4.63	$3.33x10^{-3}$	300	18.5	>90	Pulsed laser deposition
Ferum	-	$400x10^{9}$	$2.5x10^{-12}$	-		Solid state synthesis
	4.23	-	-	-	50-90	Pulsed laser deposition
Chromium	3.8	-	-	-	-	Chemical precipitation

The use of SrSnO3 is visible in the area of photocatalysis. This process has helped in solving the trouble of environmental pollution and energy collapseby assisting in disintegration of contaminants and water-splitting. Usually materials used as photocatalysts need to have elevated optical absorption properties, elevated surface area, elevated crystallinity, elevated chemical stability etc. Considering all these properties, high surface area is the more important feature upsetting photocatalytic activity. This problem can be solved by controlling the size, shape and morphology of the photocatalyst[23].

Usually, photocatalytic reaction has three procedures such as: optical absorption, migration of charge carriers and catalytic reaction at the crystalline surface structure. Consequently, there are many important features for influencing the photocatalytic activity such as: the optical absorption ability, surface area, particle size and crystallinity. The generation of charge carriers are greatly improved by elevated optical absorption capability. Huge surface area makes it likely for more water molecules to be adsorbed.

Alkaline earth stannates of perovskite structure for example SrSnO3 are greatly used in energy and environment. Apart from this area of application, there are some other areas of application like in dye sensitized solar cells,lithium ion batteries, high temperature humidity sensors. It is this high photocatalytic activity that is making $SrSnO_3$ to be a good candidate for photocatalysis. The spatial structure ofSrSnO3 makes itsphotocatalytic activity helpful.The spatial structure has three dimensional network of corner-sharing SnO_6 octahedral can help charge carriers to move more easily and the octahedral tilting distortion has an optimistic outcome on local charge separation.

The photovoltaic performance of $SrSnO_3$ nanoparticles is used as electrode material in DSSCs[24].

In characterizing $SrSnO_3$, there was discovery of the crystal structure of the synthesized powder by using XRDshown in fig.13 below. Likewise, the study of micro-structures and morphologies was done using Field-emission scanning microscopy (FESEM)as shown in fig.14 below. The (TEM) was taken at a highly increasing voltage of 300Kv as shown in fig. 15 below. The UV-vis diffuse reflectance spectra were projected via a UV-vis spectrometer. Besides, the use of Raman spectroscopy and X-ray photoelectron spectroscoscopy (XPS) provides the structural idea. The selected area electron diffraction (SAED) pattern shows that multiple particles are put into aperture. Fig. 16 below shows this SAED pattern. This is orthorhombic phase of $SrSnO_3$.

The measured d spacing of 0.284 nm and 0.232 nm correspond to the 200 and 022 planes of orthorhombic $SrSnO_3$ respectively. The lattice image, depicted in fig. 16 below, reveals that SSO nanoparticles are greatly crystalline. Fig. 17 (d) shows predominantly that every primary particle (every spherical nanoparticle) is single crystalline.

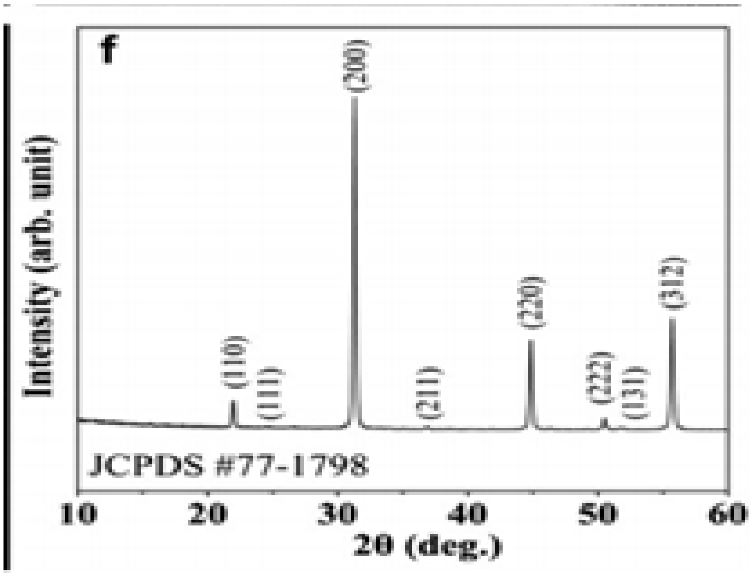


Fig. 13: XRD pattern of theSrSnO$_3$

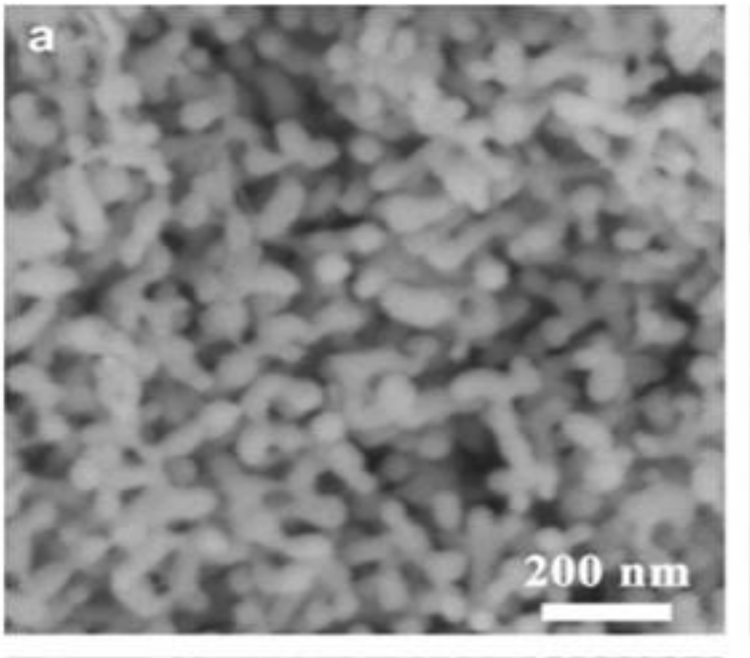


Fig. 14: the FESEM image of SrSnO$_3$

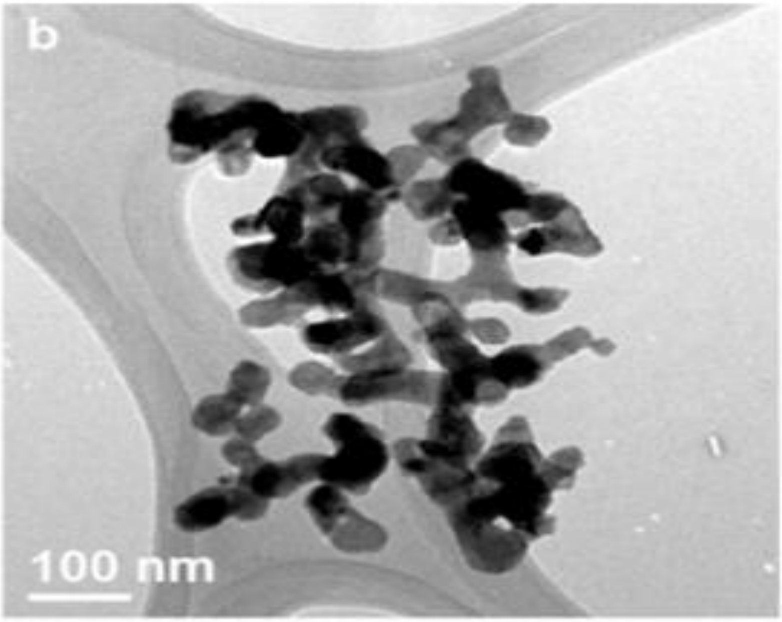


Fig. 15: The TEM image of $SrSnO_3$

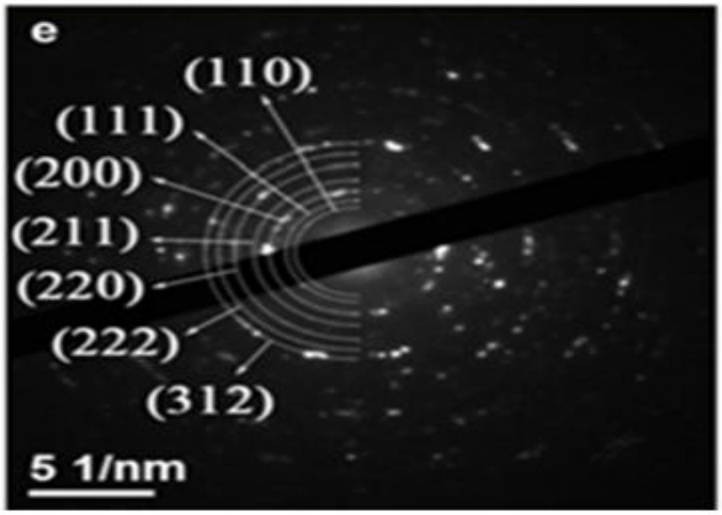


Fig. 16: SAED image of fabricated $SrSnO_3$ nanoparticles

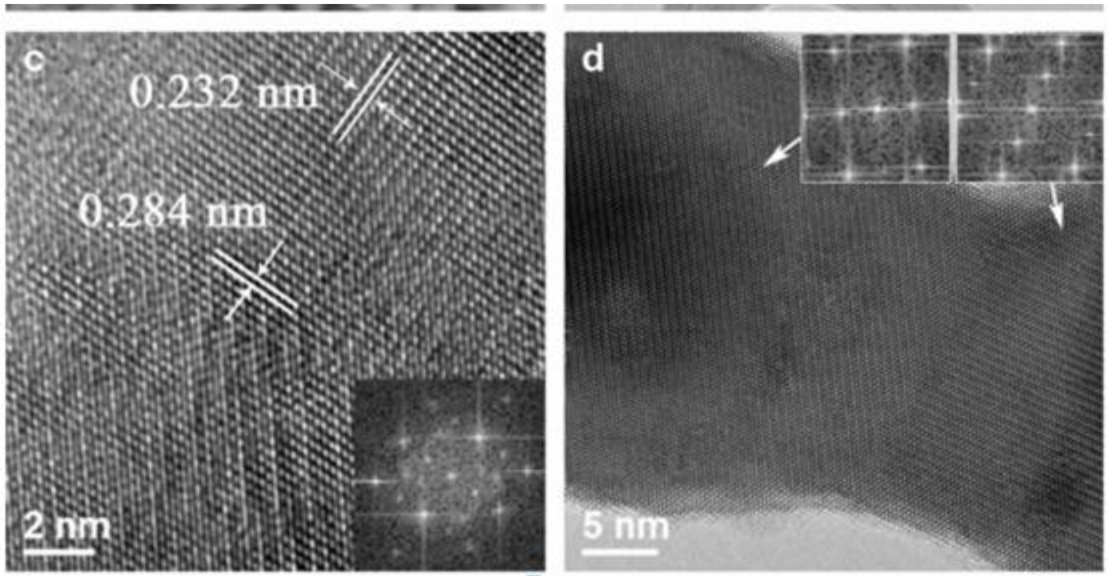


Fig. 17: HRTEM image of deposited $SrSnO_3$ nanoparticles.

5.3 Zinc Stannate, or Zinc Stannic oxide (ZSO) or Zinc Tin Oxide (ZTO)

ZSO is of spinel structure belonging to alkaline-earth stannate class. It is not a perovskite type but can be an alternative to perovskite substance[25]. It has a non-cubic spinel structure which belongs to R3c space classwhich is depicted in fig.18 below. . Its lattice constant is α=7.758 Å.

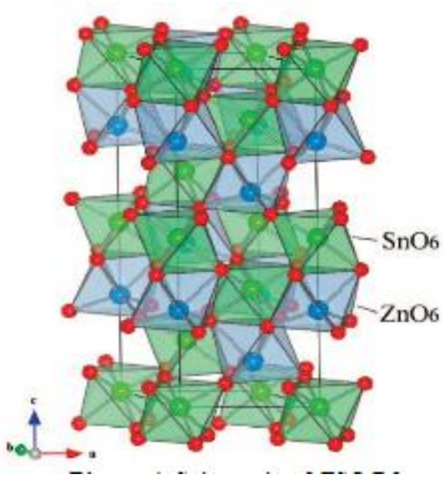


Fig. 18: The spinel structure of a rhombohedral pattern of R3c group

ZTO is an n-type material with an exceptional electronic and optical property. It has spinel non-cubic structure. ZTO has large 3.6 eV and 2.0 values of band gap energy and refractive index respectively. Its larger band gap makes it to have better photostability against UV light than even binary and other stannate components. It is of high-speed charge injection with fast electron flow. It also has soaring electron mobility (10 – $15Cm^2V^{-1}S^{-1}$) and finally first-class light-harvesting properties. ZTO metal oxide semiconductor particles are identified for having steady properties under severe situation. They have their use generally in making photo anodes given that theyhave large surface area and elevated porous structure. This helps in absorbingdye into semiconductor material.

When doped,ZTO or ZSO which has non-cubic structure would retain excellent transparency making it good candidate transparent conductor. Transparent conductors are materials with DC electrical conductivity but transparency to light over a wavelength range of interest. These materials are important in solar photovoltaics, displays and technologies. The most commonly used material is the n-type oxide, In_2O_3 doped with Sn (ITO). This material has excellent performance. However, there is an interest in finding alternative materials. This is both because of cost issues associated with a material having a large concentration of In and because of interest in finding materials with higher performance or different properties that may be enabling for new technologies. For example, it would be desirable to find p-type material that could be used in transparent electronics, materials that operate in different wavelength ranges, or materials that have different mechanical properties and materials compatible with different active electronic material eg, organic or oxide electronics.

The challenge led to a recent proposal of many new materials, one of which is n-type cubic perovskite $BaSnO_3$. The material has a number of advantages. These include the fact that it is In free. It has been shown above that the related compounds, n-type $SrSnO_3$and $ZnSnO_3$ which have smaller lattice parameters, are more compatible with common oxideelectronic substrates.

It has many promising applications in gas sensors, electrode of solar cells, in DSSC photocatalysts and negative materials for rechargeable Lithium ion batteries[26].

Even though ZSO is of non-cubic structure, it can maintain admirable transparency when doped with an appropriate dopant. This makes it a good material for transparent conductor.

Considering it in R3c group, it has inborn ferroelectric properties with elevated dielectric constants. When these are modified, it will increase the mobility when it is doped with dopable/promising dopants.

Researchers have established that ZSO is one of those prospective transparent conductive material for few decades now. But of late there is generated and regained interest in the understanding and its use in high mobilities field-effect transistors[27].

Table 3: the ZTO performance:

Dopant	Bandgap (eV)	Resistivity (Ω/cm)	Conductivity (S/cm)	Mobility ($cm^2V^{-1}s^{-1}$)	Trans (%)	Synthesis method
Undoped	3.84	-	-	-	-	Wet chemical deposition
Undoped	-	-	-	45	-	Molecular beam epitaxy
Undoped	-	$4x10^{-3}$	-	-	>80	Magnetic sputtering

ZSO is a transparent conducting oxide. Its application is greatly in DSSC. It is used as electrode material in DSSC due to its stability against acid making it better than its binary counterparts. To achieve this application inDSSC, there should be a control of the particle size to guarantee large surface area for dye absorption[28].

The ZSO nanoparticles is achieved by hydrothermal technique. This is by the decomposition of combination of zinc and tin tert-butylamine complexes. There were five solar cell dyes of the same thickness (~ 4.3 µm) with different sensitization times used in this technique. The adsorption increases fast with sensitization time and later become saturated. The short circuit current density (J_{sc}) equally increases fast as sensitization time increases and later become saturated. The open circuit voltage (V_{oc}) and fill factor (ff) are stable with diverse sensitization times[29]. This shows that ZSO is stable against acidic dye molecules. All films fabricated from ZSO were transparent. The highest energy conversion efficiency got from a ZSO cell is 3.8 % with film thickness of 5.6 µm wich is near to the highest reported efficiency ever achieved of about 4.5 %. However, the major setback for ZSO cell is the short electron diffusion length with increased film thickness. A higher dye loading on a ZSO film, the electron injection as well as transport ought to be poor. It is expected to have low open-circuit voltage.

The product got was characterized with XRD. TEM, SAED,

The fig.19below is a TEM result which shows that nearly all attained nanoparticles have size in the range of 10-60 nm. This is important since it will provide a large surface area needed in DSSC utilization.

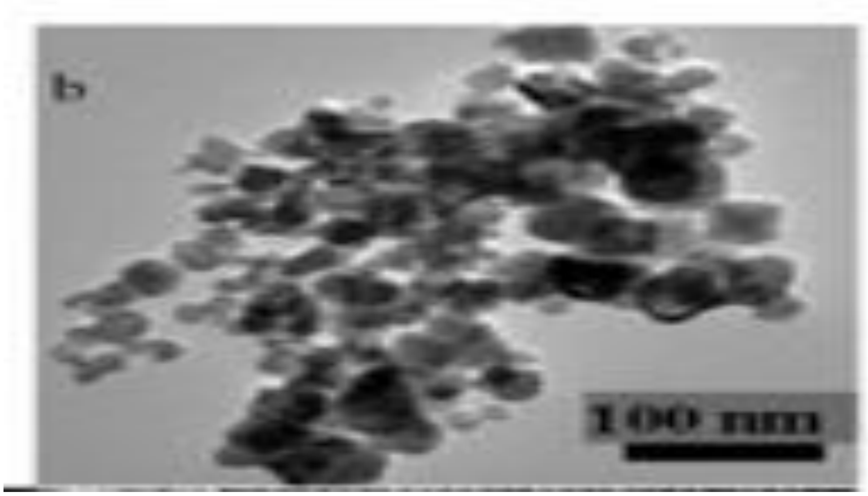


Fig. 19: The low magnification TEM image of ZSO

The XRD result shown in fig 20 indicates that the product is a pure ZSO having cubic inverse-spinel crystal structure with average crystal size of about 20 nm

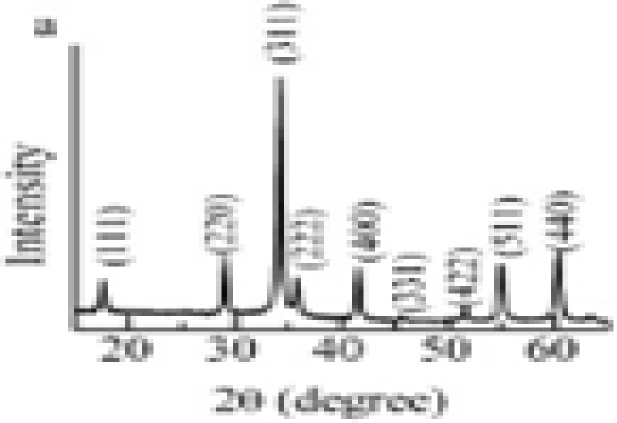


Fig. 20: The XRD patter of ZSO

The fig. 21 and fig 22 below shows the selected-area electron diffraction (SAED)pattern and high resolution TEM of ZSO which further confirms the crystallinity of the ZSO nanoparticles.

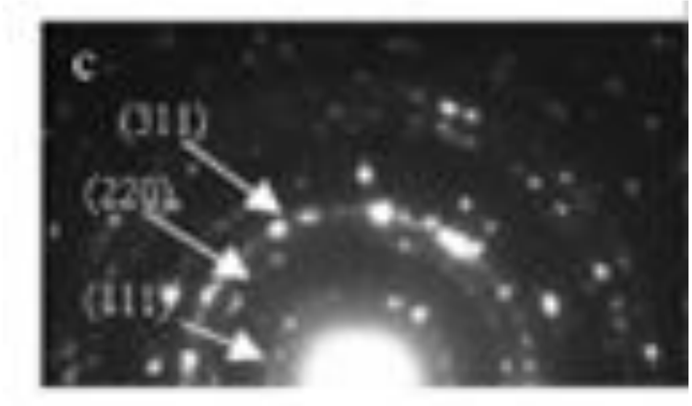


Fig.21: The SAED image of ZSO nanoparticles.

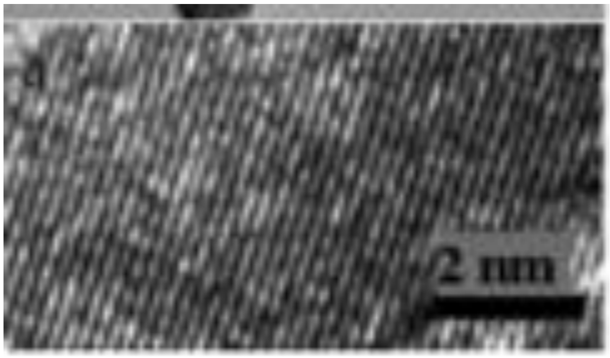


Fig. 22: The high resolution TEM of ZSO

6.0 Preparation/method of synthesis

Stannate powders (the three under consideration in this book) couldbe fabricatedvia environmentally welcomingmethod whether or not in monophasic state. The character of alkaline-earth metal source on the phase purity of various metal stannates is of immense influence.

Alkaline earth orthostannates (A_2SnO_4)has sprouted great interest in researchers for novel phosphorus resulting to their stable crystalline structure as well as elevated physical and chemical stability. Hence the need to fabricate them.

There are numerous methods used in the fabrication of stannates such as: sol-gel, high temperature solid state reaction, sol-gel combustion, hydrothermal, polymer precursor, spray pyrolysis, lyothermal, wet chemical, chemical precipitation and reverse micelle, magnetic sputtering etc. Out of all these techniques, solid state reaction fabricating means is used in this work together with hydrothermal. This is because it is a better and a convenient technique due to the fact that it is simple, have better mixing of starting materials, have relatively little reaction temperature and simple control of the chemical composition of the end product.

The fig. 22 below showdifferent synthesis methods used in fabrication of thin film stannates and other materials.

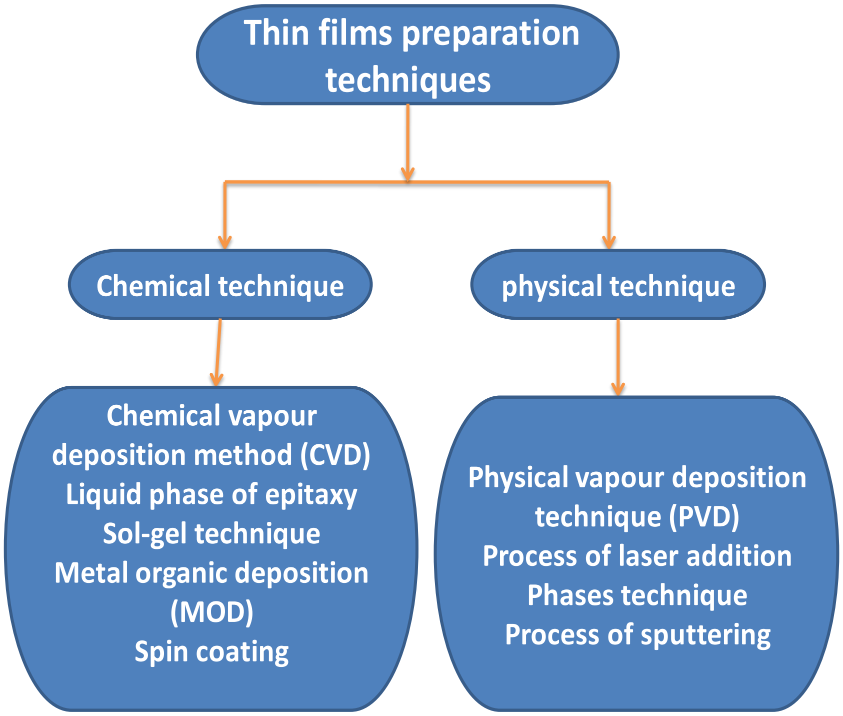


Fig.23: Common techniques for thin filmpreparation

Effective deposition of stannates Nanopowders via a chemical or physical route depicts good structure for doping.

The metal oxide semiconductor thin films are synthesized via varieties of processes on working active layer materials with stable interfaces.

6.1 Thin films:

Substances that are made to be thin films are easily integrated into differentdevices. The uniqueness of such substancessignificantlyvary when they are examined as thin films. The bulk of the working substances are ratherimportant in thin film structure due to someparticularproperties such as: electrical, magnetic, optical characteristics or wear resistance. In the technology of thin film, there is the utilization of the idea that the properties canhabituallychecked by the thickness factor. Through deposition processes, thin films are made either by physical or chemical techniques.When thin films are synthesized, they have applications in microelectronic and optoelectronics appliances (these devices belong to the supreme hi-tech movers of our economy). They are equally applied in magnetic thin films in recording devices, creation and maintenance of energy, display and storage applications, magnetic sensors, gas sensor, coating of all kinds, bio-technology, photoconductors, IR detectors, interference filters, solar cells, polarizer's, temperature controller in satellite, superconducting films, communication and information processing, anticorrosive and decorative coatings. Thin film practices have been thoughts fixed in material science and engineering.

6.2 Metal oxide thin films:

Metal oxides are made up of positive metallic and negative oxygen ions. Strong ionic bond is attained when the metallic and oxygen ions are bound by electrostatic interaction. The majority of the metal oxides confirmed outstanding thermal and chemical steadiness. Their severaloutstandingcharacteristics resulting from partially or fully filled d-shells help in all kinds of electronic device usages such as solar cells, photoelectrochemical cells, thin film transistors, photocatalysts, and sensors. With reduction in material dimension and bulk up to nanoscale level, this electronic qualities will be improved.

The characteristicqualities of metal oxides thin films show them as being fascinating. They played a big role in the enhancement of modern discovery of optics, sensors, photocatalysis, electro catalysis, anticorrosion, electronic and magnetic utilizations. The interesting physical distinctivenessobserved in nanoscale metals as well as semiconductors are related toalterations in electronic structure as well as the vast surface-to-volume ratios, which make them distinctlydifferent fromcomparable bulk solids. Breathtaking power over materials dimension, figure, as well asinconsistency in the nanometer length scale is being permitted the enhancement of synthetic measures resulting from their extraordinarycharacteristics. There is construction of nanoparticle assemblies in the solid state given that the practice expected and devices that are projected to be created cannot be solution based or single particle based.Consequently, development of measures for assembling of nanoparticles into solid state structures, as keeping their characteristic physical traits, becomes a noteworthysetback.

There have been a number of different approaches to reduce high cost PV solar cells over the last decade, notably the thin film approaches, but to date they have been limited application due to variety of practical problems. Thin film solar cell is a third generation solar cell. The thin film approaches gave birth to DSSCs and others which can be of perovskite or spinel nature/type. This is drawing great deal of investigative attention on how best to improve it.

The synthesis and studies of nanosized materials is importance because of their characterization interest and their interesting properties such as catalytic, thermal, magnetic, electrical and optical characteristics plus the range of applications associated with them. Research into oxide thin films is being importunate since 1960s; however, it was the discovery of soaring temperature superconductivity in 1986 which gave a key motion to the research in the area of multi-component complex oxide thin films. These oxides are the focus of scientific studies since they signify enormous promise for the 21st century solid state devices.

These thin films could be synthesized using diverse processes as shown in the diagram below. But our work will be based on chemical methods with instance on solid state reaction and hydrothermal techniques.

Conclusion

They stannates have varieties of ways that they can be prepared but here the predominant process are solid state reaction and hydrothermal processes. The stannates,typically perovskite-type or spinel-type areutilized in solar cells,(alternative materials, photoanodes,future transparent conductive tool etc), photocatalysts, etc. Its synthesis improvement is a pointer that its optical as well as electrical performance could be advanced. Doping stannates(which has revealed a significant performance as hopeful) offers a further alternative when doped with the right material.If dopedwith certain right dopants helps in gettting high electron mobility, making the resistivity which is a reflection of conductivity to be lowwith high band gap, etc. The incorporation of doped stannates into solar energy harvesting devices helps in solving world energy problems by making the solar cells have a very high functional performance.

References

[1] A. Gaurav, S. Madhungiri and F. Karale, "High solar energy concentration with a fresnel lens.," *A Review,* vol. 2, no. 3, pp. 1381-1385, 2012.

[2] S. P. Sukhatme, "Solar Energy", Tata McGraw Hill publication.

[3] S. Shruti, K. Kamlosh and S. Asutosh, "Solar cells in research and applications," *Material sciences and applications,* vol. 612113, pp. 1145-1155, December 2015.

[4] Wang, L.; Fang, X.; Zhang, Z., ""Design methods for large scale dye-sensitized solar modules and the progress of stability research"," *"Renewable and Sustainabl Energy Reviews",* vol. 14 (9), pp. 3178-3184, 2010.

[5] L. Wang and W.

[6] I. Affrin, Solar energy harvesting and its applications, Ladydoak college, Madurai.

[7] M. Patel, "Wind and solar power plants", CRC Press, 2016.

[8] S. Arms, C. Townsend and D. e. a. Churchill, ""Energy harvesting, wireless, structural health monitoring and reporting system"," in *in preceedings of the 2nd Asia Pacific Workshop on SHM*, Melboune, Australia., December,2008.

[9] W. Lee, H. Kim, J. Kang, D. Jang, T. Kim and J. Lee, "Transparent perovskite barium stannate with high electron mobility and thermal stability," *Annual review of materials research.,* vol. 47, pp. 391-423, 2017.

[10] .. Park, "perovskite solar cells: an emerging photovoltaic technique," *Materials today,* vol. 18, no. 2, pp. 65-72, 2014.

[11] W. Bragg, "The structure of the spinel group of crystals.," *Philosophical Magazine Series 6,* vol. 30, pp. 305-315, 1915.

[12] W. Yang, J. Noh, N. Joen, Y. Kim, S. Ryu, J. Seo and S. Seok, "High performance photovoltaic perovskite layers fabricated through intramolecular exchange," *Science,* vol. 348(6240), pp. 1234 - 1237, 2015.

[13] Q. Liu, H. Li, B. Li, W. Wang, L. Q., Y. Zhang and J. Dai, "Structure and band gap engineering of Fe-doped SrSnO3 epitaxial films," *EPL (Europhysics letters),* vol. 108(3), p. 37003, 2014.

[14] K. Rao and Vanaja, "Influence of transition metal (Cu,Al) ions Doping on Structural and optical properties of ZnO nanopowders," in *materials today: proceedings*, 2015.

[15] K. Karunakaramoorthy and G. Suresh, "Synthesis and characterization of the Al- doped and Al-Mn Co-doped Zno Nanoparticles by sol-gel method," *555Xresearch2,* vol. 4, no. 7, July 2014.

[16] Y. D. Zhang, X. M. Huang, D. M. Li, Y. H. Luo and Q. B. Meng, ""How to improve the performance of dye-sensitized solar cell modules by light collection," *Solar energy materials and solar cells,* vol. 98, pp. 417-423, 2012.

[17] S. Raghavan, T. Schumann, H. Kim, C. T. Zhang and S. Stemmer, "High mobility BaSnO3 grown by oxide molecular beam epitaxy.," *APL Materials,* vol. 4(1), p. 016106, 2016.

[18] J. John, V. Pillai, A. Thomas, R. Joseph, S. Muthunatesan and R. Prabhu, "Synthesis, structural and morphological property of BaSnO3 nanopowder prepared by solid state ceramic method," *material science and engineering,* vol. 195, p. 012007, 2017.

[19] J. Li, Z. Ma and K. Wu, "Improved thermoelectric power factor and conversion efficiency of perovskite barium stannate," *RSC Advances,* vol. 7(52), pp. 32703-32709, 2017.

[20] W. Lee, H. Kim, J. Kang, D. Jang, T. Kim, J. Lee and K. Keem, "Transparent perovskite barium stannate with high electron mobility and thermal stability.," *Annual Reviews of Materials Research,* vol. 47, pp. 391-423, 2017.

[21] Y. Zang, J. Wang, M. Sahoo and T. K. T. Shimada, "Strain induced ferroelectricity and lattice coupling in BaSnO3 and SrSnO3," *Physical chemistry chemical physics.,* vol. 19(38), pp. 26047-26055, 2017.

[22] C. Lee, D. Kim, I. Cho, S. Park, S. Shin, S. sEO and K. Hong, "Simple synthesis and characterization of SrSnO3 nanoparticles with enhanced photocatalytic activity," *International journal of hydrogen energy,* vol. 37, pp. 10557-10563, 2012.

[23] H. chen and N. Umezawa, "Sensitization of perovskite strontium stannate SrSnO3 twards visible-light absorption by doping," *Photocatalysis and photoelectrochemistry for solar fuels,* 2014.

[24] K. Ong, X. Fan, A. Subedi, M. Sulivan and D. Singh, "Transparent conducting properties of SrSnO3 and ZnSnO3," *Applied physics letters,* vol. 3, no. 6, pp. 10,1063-1,4919564, 2015.

[25] T. Minami, H. Sonohara, S. Takata and H. Sato, "High transparent and conductive zinc-stannate thin films prepared by RF magnetron sputtering," *Japanese journal of applied physics.,* vol. 33(12A), p. L1693, 1994.

[26] A. Sharma, Y. Kumar and P. Shirage, "Structural, optical and excellent humidity sensing behaviourof ZnSnO3 nanoparticles: effect of annealing.," *Journal of materials science: materials in electronics,* pp. 1-15, 2018.

[27] B. Tan, E. Toman, Y. Li and Y. Wu, "Zinc stannates (Zn2SnO4) Dye- Sensitized Solar Cells," *Journal of American Chemical Society,* vol. 129, pp. 4162-4163, 2007.

[28] B. Tan, E. Toman, Y. Li and Y. Wu, "Zinc stannate dye-sensitized solar cells," *JACS,* 2007.

[29] P. Das, A. Roy and P. Devi, "Zn2SnO4 as an alternative photoanode for dye sensitized solar cells: current status and future scope.," *Trans. industrial ceramic society,* vol. 75(3), pp. 1-8, 2016.