Fabrication of Stannate Perovskite Structure as Optoelectronics Material: An Overview

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Abstract. This paper presents a review of recent fabrication progress of perovskite-type material suited for the future optoelectronics applications. Wide varieties of optoelectronic devices include solar cell, liquid displays, transparent FETs, etc are becoming the mainstream for future electronics global industry. In June 2015, the major breakthrough of perovskite structure in solar energy harvesting with PCE of 20.1% has achieved. Since then, numerous research has been conducted progressively to further enhance the performance of the perovskite structure as new alternative materials for optoelectronics applications. The perovskite-type oxide is having typical ABO3 crystallized structure. It is one of an important class of materials that have many exceptional physical properties such as superconductivity, colossal magnetoresistance, ferromagnetic, piezoelectric, high-transition-temperature superconductivity, ferroelectricity, piezoelectricity, and photoelectrochemical sensitivity. In this paper, we reviewed development progress one of the major classes of perovskite-type materials namely Stannate-based. Calculated data from simulation results such as DFT and first principle were excluded and only fabricated devices are covered in this paper.

1. Introduction
Wide varieties of optoelectronic devices include solar cell, liquid displays, transparent FETs, etc are becoming the mainstream for future electronics global industry. In June 2015, Woon has created a breakthrough in perovskite structure in solar energy harvesting with PCE of 20.1% [1]. Since then, numerous research has been conducted to further enhance the performance of the perovskite structure as an alternative for optoelectronics materials. The perovskite-type oxide is one of an important class of materials that have many exceptional physical properties such as superconductivity, colossal magnetoresistance, ferromagnetic, piezoelectric, high-transition-temperature superconductivity, ferroelectricity, piezoelectricity, and photoelectrochemical sensitivity [2-3]. Moreover, due to their similar pseudocubic crystal structures and matching lattice hence they can be fabricated into devices with perovskite-type heteroepitaxial structures [2]. The perovskite-type oxides have simple and flexible structures that cater to ionic substitution, carrier doping, and oxygen non-stoichiometry. Therefore, they prominently technologically important materials for a wide variety of industrial optoelectronics [2]. The quest for finding new alternative materials is very much related to the cost issues associated with the scarcity of Indium. Furthermore, the interest in finding alternative materials
that having different properties may be the enabling factor for new technologies advancement soon [4].

For Transparent Conductive Oxide (TCO), obtaining the best performance of highly transparent and low in resistivity is the toughest challenge because in nature the highly transparent materials are prone to become insulators that having very low in conductivity. Most of the current market TCO devices are dominated by Indium based. It has very excellent performance with wide bandgap more than 3 eV, resistivity as low as $10^{-5} \Omega \text{cm}$ and transmittance as high as 90%. However, the shortage of Indium supply has continued pushing the manufacturing cost higher and higher. The plan is to find alternative material which is Indium free n-type transparent conductive. Hence, the developments of new TCO will require modification in low-cost materials properties and fabrication techniques to enhance their optical and electrical characteristics. In which it will cater to the special needs in transparent electronics devices such as transparent conductors, transparent transistors, light-emitting devices, and transparent capacitors. The perovskite-type material is having $\text{ABO}_3$ crystal structure. Both A and B are consists of cations which feasible to be substituted with suitable dopant at either A or B site to improve the optoelectronic performance. One of the challenges is to grow the layer of a thin film with very low densities of grain and domain boundaries which contribute to limit the conductivity performance [4]. The major threat is the intrinsic poor charge carrier mobility of the most perovskite oxides which typically 1~10 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature [5]. Accordingly, with the substitution of the suited cation usually will lead to the donation of charger carriers to the conduction band [6].

2. Stannate Based Materials

The stannate based perovskite-type is having the general formula of $\text{ASnO}_3$. One of the major class material is falls under the group of alkaline-earth stannate for which the A site to be occupied by either $\text{Ba}$, $\text{Sr}$ or $\text{Ca}$ with the ionic radius of 135 pm, 118 pm, and 100 pm respectively [7]. Despite they possess wide optical band gaps the electron conductivity is remarkably superior [3]. They are also broadly used in electronic industries due to their incredible dielectric and gas sensing properties [8]. Alkaline earth stannates attract much technological interest due to their applications in transparent conductive is provable. They have been utilized majorly in the fabrication of transparent electrodes for various application particularly in photovoltaic cells and organic light-emitting diodes [9]. This material also has been reported to be used in numerous sensors development [4].

2.1. Barium Stannate Oxide, $\text{BaSnO}_3$ (BSO)

The BSO is an n-type material with having cubic perovskite structure belongs to Pm$\bar{3}$m space group with a lattice constant of $a = 4.139$ Å [10] as illustrated in Figure 1. It is dopable to a highly conductive state using Sb or La [11]. Highest performance for TCO BSO doped La (BLSO) has shown excellent metallic conduction [12] as shown in Table 1. Surprisingly, the BLSO is not only own superior performance for its mobility but it also very stable to sustain at higher thermal condition [13]. In contrast, the epitaxial form of BSO is still having lower mobility. This is due to grain boundaries and dislocation which causes charge traps and scattering hence reducing the carrier density and mobility simultaneously [14]. Thus, mobility in thin films will be improved when dislocation and grain boundary reduced for example by choosing the lattice-matched substrate [15]. A modified MBE technique is introduced by replacing the typical Sn metal source with pre-oxidized $\text{SnO}_2$ so that more precise stoichiometry control in MBE process of La-doped $\text{BaSnO}_3$. The modified MBE technique has successful push the mobilities performance increased twice by any.
other reported method [16].

Table 1. The Barium Stannate Oxide (BSO) Performance.

| Dopant   | Bandgap [eV] | Resistivity [Ω/cm] | Conductivity [S/cm] | Mobility [cm²V⁻¹s⁻¹] | Trans [%] | Fabrication Method                | Ref. |
|----------|--------------|---------------------|---------------------|-----------------------|-----------|-----------------------------------|------|
| Lantahnum| 4.05         | 5.9x10⁻⁴            | 1695                | 103                   | -         | Solid state reaction              | [12] |
| Lantahnum| -            | 10x10⁻⁴             | 100                 | 320                   | -         | Solid state reaction (single crystal) | [13] |
| Lantahnum| -            | -                   | -                   | 70                    | -         | Pulse laser deposition (epitaxial films) | [13] |
| Lantahnum| -            | -                   | -                   | -                     | -         | Modified MBE                      | [16] |
| Lantahnum| 3.95         | -                   | -                   | 150                   | >80       | Sol-gel                           | [28] |

2.2. Strontium Stannate Oxide, SrSnO₃ (SSO)

The SSO has an orthorhombic perovskite structure belongs to Pbnm space group with the pseudocubic lattice constant of \(a = 5.709\ \text{Å}, \ b = 5.703\ \text{Å} \text{ and } c = 8.065\ \text{Å} [17]\ and a wide bandgap of 4.27 eV [6] as illustrated in Figure 2. It was reported to be classified as n-type material [18]. The orthorhombic distortion of the perovskite structure in SSO leads to absorption in the visible as the doping level is increased [18]. The smaller lattice parameters are more compatible with common oxide electronic substrates. The SSO much struggle for its lower mobility performance as compared to BSO perovskite. Nevertheless, the same group Liu [19] has created a big heap of achieving 18.5 cm²V⁻¹s⁻¹ mobility by introducing Ta as dopant [20] as shown in Table 2. As Ta content increases the carrier concentration and ionization efficiency will also increase thus lowering the potential barrier [21]. Because of that, mobility has extremely improved by 50 fold from the previous achievement.

Figure 2. Schematic of SSO Pbnm Orthorhombic Structure [35].
Table 2. The Strontium Stannate Oxide (SSO) Performance.

| Dopant       | Bandgap [eV] | Resistivity [Ω/cm] | Conductivity [S/cm] | Mobility [cm²V⁻¹s⁻¹] | Trans [%] | Fabrication Method | Ref. |
|--------------|--------------|--------------------|---------------------|-----------------------|-----------|--------------------|------|
| Erbium       | -            | 0.1x10⁻⁵           | 1x10⁰               | -                     | -         | sol–gel            | [9]  |
| Stibium      | 4.53         | 23x10⁻³            | 43.48               | 0.329                 | >90       | pulsed laser deposition | [19] |
| Neodymium    | -            | 21x10⁻³            | 47.62               | 0.104                 | >90       | pulsed laser deposition | [20] |
| Tantalum     | 4.63         | 3.33x10⁻³          | 300                 | 18.5                  | >90       | pulsed laser deposition | [21] |
| Ferum        | -            | 400x10⁹            | 2.5x10⁻¹²           | -                     | -         | solid state synthesis | [30] |
|              | 4.23         | -                  | -                   | -                     | 50–90     | pulse-laser deposition | [31] |
| Chromium     | 3.8          | -                  | -                   | -                     | -         | chemical precipitation | [32] |

2.3. Calcium Stannate Oxide, CaSnO₃ (CSO)

The CSO is having distorted orthorhombic perovskite structures belongs to Pbnm space group with the lattice constant of $a = 5.4941$, $b = 5.6760$, and $c = 7.9280$ [22] as illustrated in Figure 3. It has a very wide direct bandgap of 4.95 eV to 5.38 eV [23] as shown in Table 3. The CSO has been seen predominantly in photoluminescence materials [22, 24]. In fact, the electrical properties of CSO perovskite are not much appeared in the literature. Nonetheless, epitaxial CSO films with various thicknesses were able to grow on LAO(001) single crystal substrates through a pulsed laser deposition method [23]. Most probably the CSO is not much in interest for its electrical properties is due to it exhibits p-type conduction [25].

Table 3. The Calcium Stannate Oxide (CSO) Performance.

| Dopant       | Bandgap [eV] | Resistivity [Ω/cm] | Conductivity [S/cm] | Mobility [cm²V⁻¹s⁻¹] | Trans [%] | Fabrication Method | Ref. |
|--------------|--------------|--------------------|---------------------|-----------------------|-----------|--------------------|------|
| Europhium    | 4.10         | -                  | -                   | -                     | -         | sol–gel            | [22] |
| undoped      | 4.95-5.38    | -                  | -                   | -                     | -         | pulsed laser deposition | [23] |
| Terbium-Magnesium | -      | -                  | -                   | -                     | 80        | RF sputtering method | [24] |
| Scandium     | 4.4          | -                  | -                   | -                     | -         | solid state reaction | [25] |

Figure 3. Schematic of CSO Pbnm Orthorhombic Structure [36].
2.4. Zinc Stannate Oxide, ZnSnO$_3$ (ZSO)

Other than alkaline-earth stannate group, the ZSO also has been explored as one of the alternatives for perovskite-type material as shown in Table 4. It has a non-cubic structure belongs to a space group of R3c with the lattice constant of $a=7.758$ Å [26] as illustrated in Figure 4. Despite non-cubic, the ZSO can retain excellent transparency when doped with the right dopant which puts it as one of the potential candidates for transparent conductor [4]. Furthermore, ZSO is also inherited ferroelectric properties from its R3c group and high in dielectric constants thus modifications of it may help to push the mobility higher by doped it with possible dopant [27]. Although the ZSO has been proven as one of good potential transparent conductive material for over two decades [28] only recently it reclaim research interest in the realization of high mobilities field-effect transistors [29].

Table 4. The Zinc Stannate Oxide (ZSO) Performance.

| Dopant   | Bandgap [eV] | Resistivity [Ω/cm] | Conductivity [S/cm] | Mobility [cm$^2$V$^{-1}$s$^{-1}$] | Trans [%] | Fabrication                  | Ref.   |
|----------|--------------|--------------------|---------------------|----------------------------------|-----------|------------------------------|--------|
| undoped  | 3.84~4.64    | -                  | -                   | -                                | -         | wet chemical synthesis       | [26]   |
| undoped  | -            | -                  | -                   | 45                               | -         | Molecular beam epitaxy       | [28]   |
| undoped  | -            | 4x10$^{-3}$        | -                   | >80                              | -         | Magnetron sputtering          | [33]   |

3. Conclusion

Based on the recent fabrication progress of perovskite-type as an alternative material has shown an optimistic indicator that it can be explored further to enhance its optical and electrical performances. The Barium Stannate doped with Lanthanum (BLSO) has shown able to achieved 320 cm$^2$ V$^{-1}$ s$^{-1}$ for electron mobility despite highly transparent with bandgap more than 4 eV. The resistivity which reflects conductivity of BLSO achieved up to $10^4$ Ω/cm as compared to ITO $10^5$ Ω/cm. It then followed by SSO doped with Ta which has shown electron mobility up to 18.5 cm$^2$V$^{-1}$s$^{-1}$ and has a very wide bandgap of 4.45 eV. While the CSO possess transparent characteristics, unfortunately, mobility is very poor and prone to p-type conductor characteristics. Even though the ZSO is not classified under alkaline group, it can provide exceptional mobility even at the undoped form with values reaching up to 45 cm$^2$ V$^{-1}$ s$^{-1}$. This also provide another promising alternatives with the help of appropriate doping materials. Overall, the BLSO has shown a remarkable performance as promising alternative material to indium based as perovskite stannate structure for future transparent conductive devices. This supported by the fact that the BLSO is having a proper lattice arrangement with an ideal Pm$\overline{3}$m cubic structure as compared to others in its group.
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