

Barium Stannate Nanoparticle: Synthesis, Properties and Application

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Abstract

Alkaline earth stannates have garnered increased interest as possible materials for applications such as ceramic capacitors, gas sensing, and transparent conducting oxides. To create BaSnO_3 powders with micron-sized grains, a noble wet chemical method is used. Various approaches have been used to address issues with irregular grains and inadequate densification in the traditional solid state pathway. At 150–450 °C, barium stannate demonstrated n-type semiconductor behaviour, with activation energy reliant on the annealing temperature of the material. The types of ionosorbed oxygen species that were most prevalent were estimated. It was demonstrated that when the temperature rose, they transitioned from molecular to atomic species. Nanocrystalline SnO_2 -based sensors were used as reference sensors in a comparative examination of sensor response to different inorganic target gases. In contrast to SnO_2 , BaSnO_3 showed greater sensitivity to SO_2 while having a surface area that was an order of magnitude less. It was discovered that the enhanced sensitivity of BaSnO_3 to ppm-range concentrations of SO_2 in air was caused by barium-promoted sulphate production favouring target molecule oxidation.

I. Introduction

Due to its potential uses in thermally stable capacitors, photocatalysis, and chemiresistive sensor materials for toxic and noxious gases, barium stannate (BaSnO_3), a member of the family of alkaline earth stannates with the general chemical formula MSnO_3 ($M = \text{Ca}, \text{Ba}, \text{Sr}$), has been extensively researched (Kocemba et al., 2007; Gao et al., 2023). With a lattice parameter that varies slightly depending on the synthesis method, it stabilises in a cubic perovskite structure at room temperature (space group $\text{Pm}\bar{3}\text{m}$). It behaves like an n-type semiconductor, with an optical band gap reported to be between 3.1 and 3.4 eV. In order to improve the sensor response for a variety of target gases, such as NH_3 , Co, H_2 , Cl_2 , LPG, ethanol, NO_x , humidity, O_2 , etc., BaSnO_3 (BSO) compositions have been extensively studied (Cerdea et al., 2002; Doroftei et al., 2012).

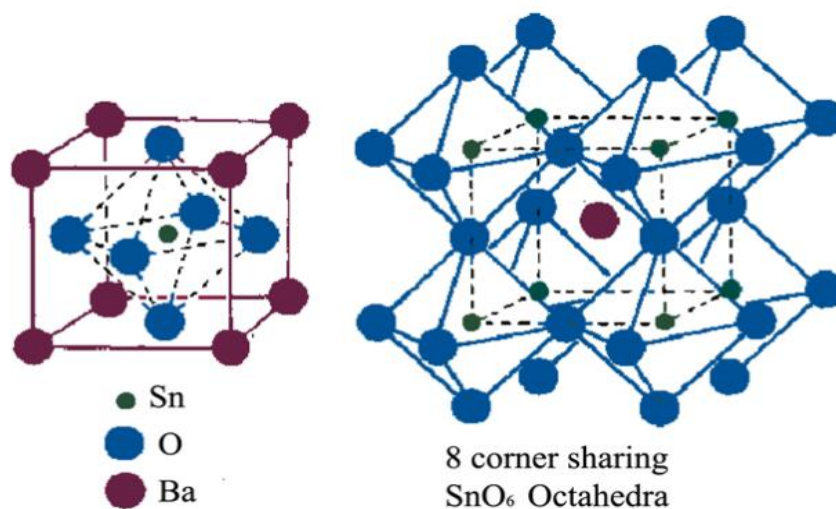


Fig 1: Perovskite structure of BaSnO_3

Fig. 1 depicts the structure of BaSnO_3 . The structure of BaSnO_3 is a cubic perovskite. In this case, the corners of the unit cell are occupied by Ba^{2+} ions, the body centre is occupied by Sn^{4+} ions, and the face centres are occupied by O^{2-} ions. As a result, Sn^{4+} and Ba^{2+} are coordinated with six and twelve O^{2-} ions, respectively. Conversely, an O^{2-} ion has a coordination number of 2 with Sn^{4+} and 4 with Ba^{2+} . Sn^{4+} fills one-fourth of the

octahedral vacancies in the tight cubic close packing of the O^{2-} and Ba^{2+} ions. A three-dimensional structure is created by joining eight $[SnO_6]$ octahedrons via their corners (Wenshung, 2002).

It should be mentioned that the microstructure, density, grain size, and inherent flaws in polycrystalline ceramics are all connected to the bulk and surface electrical characteristics of the material. Therefore, several physical and chemical techniques are employed to enhance the conduction behaviour during the manufacture of BSO powder. The solid state reaction method, which was primarily used to increase densification (Upadhyay, 2013; Farfan et al., 2009), ran into issues with uneven grain development and poor densification. According to Doroftei et al. (2012), sintering in the 1200–1400 degree Celsius range was insufficient for acceptable densification, intergranular connection, and proper grain development in the solid state method. Porosity could not be eliminated by sintered BSO ceramics, even at 1600°C for 12 hours; relative density > 95% was only attained after 72 hours of sintering (Azad et al., 1998). Large anion flaws in the sintered material and the incompatibility of high temperature processing with sensor technology have been two significant issues with high temperature sintering (Soni and Bajpai, 2011). Another option is the self-heat sustained approach, which produces uniform cubical grains at 1325°C. However, the non-uniformity of grain size has not been addressed (Doroftei et al., 2012). The following chemical techniques have been reported: hydrothermal (Patil and Jain, 2012), molten salt synthesis, sol-gel (Nakagauchi and Kozuka, 2007; Song et al., 2009), sol-gel based wet chemical method (Wang et al., 2011), oxalate co-precipitation method (Gopal Reddy et al., 2001), and polymeric complex route (Yasukawa et al., 2009).

Properties

The colour of $BaSnO_3$ is light yellow. It is assumed that the sintering temperature is higher than 1600°C. Even after being sintered at 1600°C, a sample remains porous. Although $BaSnO_3$ is said to melt at 2060°C, there are some differences since it breaks down into BaO and SnO_2 around 1950°C (Wenshung, 2002). $BaSnO_3$ is non ferroelectric and paraelectrical.

Applications

Barium stannate ($BaSnO_3$) nanoparticles have many applications, including:

Photoelectrochemical water splitting: $BaSnO_3$ nanoparticles' broad bandgap, minimal charge recombination, and high electron mobility make them suitable for photoelectrochemical water splitting.

Organic dye degradation: $BaSnO_3$ nanoparticles can be used to degrade organic dyes.

Photovoltaic applications: Photovoltaic uses of $BaSnO_3$ have been researched for many years. The photovoltaic efficiency of dye-sensitized solar cells (DSSCs) can be enhanced by coupling $BaSnO_3$ nanoparticles with titania (TiO). Using a straightforward sol-gel technique, the barium stannate ($BaSnO_3$, or BSO) nanoparticles were created. A varying weight percentage of titania was then added to the BSO, and the mixture was calcined at 500 °C. $TiO_2@BSO$ (TBSO) band gap values increase with the addition of titania. The produced materials were used as photoanodes in DSSCs, and photovoltaic performance was assessed at 100 mW cm^{-2} of simulated AM 1.5 G sun irradiation. The DSSC made using a pristine BSO photoanode demonstrated a power conversion efficiency that was 1.8 times lower than that of the TBSO photoanode-based DSSC. Similarly, TBSO's electron lifetime and charge collection efficiency were greater than those of DSSCs based on BSO photoanodes. The titania connecting the BSO nanoparticles improved the charge transfer and, consequently, reduced the recombination of photogenerated electron-hole pairs, which in turn improved the power conversion efficiency, electron lifetime, and charge collection efficiency. According to the study's findings, the new TBSO nanocomposite may be a good option for DSSCs based on oxide perovskites.

This is because the interconnection:

- Increases electron lifetime
- Increases charge collection efficiency
- Minimizes photogenerated electron-hole pairs recombination
- Enhances charge transfer
- Increases power conversion efficiency

Gas phase sensors: One interesting material for gas phase sensors is $BaSnO_3$. One such substance that sparked attention in gas sensor research is barium stannate (Cerda et al., 2002). It is difficult to build sensor materials using the perovskite-type cubic structure of $BaSnO_3$ by substituting cations in the Ba or Sn locations. It has been reported that n-doping, which involves partial substitution of Ba by La (Yasukawa et al., 2010) or substitution of Sn by Sb (Lu et al., 2000), or p-doping, which involves substitution of Sn by Ni, Cr, etc. (Upadhyay et al., 2007), can alter semiconductor characteristics based on the frame of $\{SnO_6\}$ octahedra.

However, by altering a complex oxide's adsorptive, acid/base, and RedOx characteristics, cation substitution may provide a variety of opportunities for surface reactivity optimisation.

According to Doroftei et al. (2012), barium stannate is a semiconductor with experimental results for an indirect band gap $E_g = 3.1\text{--}3.4$ eV and a direct optical band gap $E_g = 3.4\text{--}3.5$ eV. The band structure of BaSnO_3 is described via density functional theory (DFT) computations, with the conduction band minimum made up of antibonding Sn 5s-O 2s orbitals with Ba 6s orbitals contributing somewhat. Nonbonding O 2p orbitals make up the majority of the valence band (Moreira et al., 2012). It was discovered that the partial substitution of Sn by Sb increased the band gap; however, the band gap narrowed as the materials' calcination temperature was raised (Kufenstein and Yakuphanoglu, 2010). The requirement for harsh reaction conditions to create the perovskite structure complicates the synthesis of BaSnO_3 . Highly crystalline barium stannate, which is typically synthesised by solid-state calcinations at $T > 1200$ °C, has been thoroughly studied for its favourable dielectric qualities and its application in capacitors. BaSnO_3 was shown to be beneficial for different applications with the development of wet-chemistry synthesis approaches under moderate circumstances, such as hydrothermal and lyothermal, ion exchange, coprecipitation, or polymerised complex techniques (Lu and Schmidt, 2007). These latter include resistive gas sensors, infrared luminescence, photovoltaic, thermoelectric, and humidity detecting technologies. The detection of CO and NO showed promising sensor behaviour, but it needed a high working temperature of 450–650 °C. On the background of H_2 , CO, CH_4 , and benzene, preferred sensitivity to ethanol, hydrocarbons, and liquefied petroleum gas (LPG) was noted.

Optical applications: BaSnO_3 has been used in optical applications.

Capacitors and ceramic boundary layers: BaSnO_3 has been used in capacitors and ceramic boundary layers.

Photocatalytic H_2 production: When it comes to photocatalytic H_2 synthesis under visible light, BaSnO_3 can be employed as an electron transport booster.

The rapid surface area, broad bandgap, rapid electron mobility, and minimal charge recombination are only a few of the exceptional optoelectronic characteristics of BaSnO_3 nanoparticles. BaSnO_3 nanoparticles' suitability in a variety of technological applications is enhanced by their adjustable particle size and dispersion.

II. Conclusion

Cubic perovskite-type barium stannate was synthesized via aqueous coprecipitation with microwave-assisted hydrothermal treatment, microwave solvothermal process between $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ in a heated ethylene glycol solution as a polar solvent, etc barium metastannate nanoparticles were successfully produced. Since the microwave solvothermal reactions happened so quickly, the metal stannates were essentially heated by the exothermic reaction. Heat treatment at 800 °C for three hours produced well-crystallized BaSnO_3 nanoparticles with a fine, uniform morphology and particle sizes between 60 and 80 nm. As possible materials for gas sensing, ceramic capacitor applications, and transparent conducting oxides, alkaline earth stannates have attracted renewed interest.

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