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Investigation of Optical Properties on $BaSnO_3$ Materials

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Abstract Perovskite $BaSnO_3$ materials were synthesized under hydrothermal condition followed heat treatment at variable temperature 423 - 673 K. Phase structure and morphology and optical properties were characterized. Result showed band gap about 3.31 eV and highly optical transparency in the visible spectral region and average particles size 40 -45 nm. Thermal annealing process has affected on phase structure and luminescence in $BaSnO_3$ material.

Keywords $BaSnO_3$, Perovskite, Hydrothermal, Nano Materials

1. Introduction

The earth alkaline stannate with a chemical formula $MSnO_3$ (M= Ba, Sr, and Ca) are another perovskite system that has been used in industry for photoelectron-chemical energy conversions, stable capacitors, and gas sensors. [1-3, 14]. Among them, perovskite structured $BaSnO_3$ semiconducting material has been widely investigated on its dielectric, thermal, and photocatalytic properties as an important ceramic material [4, 5]. $BaSnO_3$ films were both highly insulating and transparent, making them potential candidates in gas-sensor applications and as insulating layers in transparent transistors. Recently, Zhang et al has suggested a possible application of $BaSnO_3$ in dye-sensitized solar cells (DSSCs) [5]. In this report the authors have demonstrated that the photon which generated electrons can be injected into the conduction band of $BaSnO_3$ from the excited $(Bu_4N)_2(Ru)(dcbpyH)_2$ dye molecules because of the energy matching levels between the excited dye molecules and the conduction band state of $BaSnO_3$. The basic structure of a DSSC has three primary parts, including the transparent anode covered by a thin layer of nano-crystalline semiconductors, the photon-adsorbed dye and a counter electrode with an electrolyte [3, 6]. In a high efficient DSSC, the band gap of the semiconductor must match with the excited energy levels of dye molecules to improve the separation of photon-generated charges and minimize their recombination [7, 11-13]. In addition, the surface microstructures, particle size and shapes, doping concentration, porosity, and film thickness of semiconductors must also be considered and optimized..

Perovskite $BaSnO_3$ has been prepared by numerous methods, such as the conventional solid state reaction route [8], coprecipitation and polymerized complex [9]. Recently, hydrothermal condition has been used for synthesis perovskite $BaSnO_3$ because this technique allows preparation of materials at low temperature, crystal structures with high quality, ultrafine particles and interesting morphologies [1-3]. In this paper, we present a study the influent of thermal annealing on phase structure and luminescence relative to defects in $BaSnO_3$ material.

2. Experimental

2.1. Chemical and Preparation

The used precursors include Tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$), barium hydroxide octahydrate ($Ba(OH)_2.8H_2O$), ammonia solution 25% (NH_4OH) are from China. $BaSnO_3$ were prepared by hydrothermal condition. A precursor of $SnO_2.xH_2O$ gel was synthesized by adding NH_4OH solution to $SnCl_4$ solution. To remove Cl^- ions the obtained gel was washed with distilled water for several times. For obtaining a sol, the washed gel was diluted to 0.3M, in which 25% NH_4OH solution as a peptisor was slowly added under stirring. Amount of the NH_4OH solution was controlled by monitoring the pH value of the mixture. The tin oxide hydrate sol was then mixed with 0.2M $Ba(OH)_2$ solution and this reaction mixture was transferred into a teflon-lined autoclave. Then the reaction container was heated up to 130^{o}C and maintained for 24h. To complete the synthesis process obtained products were washed with distilled water until pH = 7 and calcined at different temperatures from 473 up to 673 K for 5 hours in air. For the thin films samples, powder paste of $BaSnO_3$ in HNO_3 10^{-3} M and triton X – 100 were deposited on the cleaned glass substrate and heated at 150^{o}C for 1h to remove organic solvents.

2.2. Structural and Optical Measurements

The XRD pattern was recorded using an X-ray

diffractometer with Cu-kα radiation (Brucker D8 Advance, Germany). Optical absorption measurement were carried out in the wavelength range (200-800 nm) using a UV-Visible JASCO type V-670 double beam spectrophotometer. The photoluminescence (PL) and excitation spectra (PLE) were recorded using fluorolog-3 spectrophotometer with double-grating in both excitation and emission monochromators (FL3-22, Horiba Jobin Yvon). The surface morphology of the films was analyzed using scanning electron microscope equipment (FESEM, S4800 – Hitachi). All measurement was carried out at room temperature.

3. Results and Discussion

3.1. Structural and Particles Size

The phase structures of as-prepared and calcined samples were studied by XRD measurement and shown in Figure 1. As shown in this figure, XRD patterns of the calcined samples at 473, 523 K were found to be different from those of the calcined samples from 573 to 673 K. The peak positions of the as-prepared and calcined samples at 473, 523 K are only consistent with the diffraction patterns of $BaSn(OH)_6$ [10]. Meanwhile, the crystallite phases of $BaSnO_3$ were clearly observed in the samples after calcination from 573 to 673 K [19]. It suggests that hydrothermal process was necessary for $BaSn(OH)_6$ phase formation and its further transformation in $BaSnO_3$ crystallite phases during calcination. The forming of $BaSnO_3$ crystallites due to the removal of a large amount of hydroxyl groups from $BaSn(OH)_6$ complexes by thermal treatment process [10].

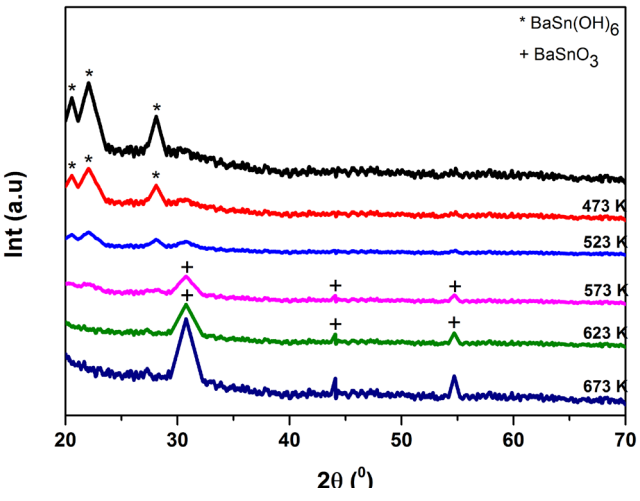

Figure 1. XRD of $BaSnO_3$ materials obtained by hydrothermal method

The crystallite size of $BaSnO_3$ has been determined by using the Scherrer formula [19].

$$\tau = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where k is 0.9, λ is wavelength of Cu-kα radiation (0.154056 nm), β is the full width at half maximum (FWHM) of diffraction peak and θ is the diffraction angle. Using XRD pattern data of $BaSnO_3$ at 623 K and equation (1) to calculate, the obtained average particles size are around 42 nm for the calcined $BaSnO_3$ at 623 K sample. Moreover, scanning electric microscope image of $BaSnO_3$ thin film in Figure 2 showed also its typical morphology with uniform particles with average size about 40 – 45 nm, this is consistent with that calculated by using equation (1).

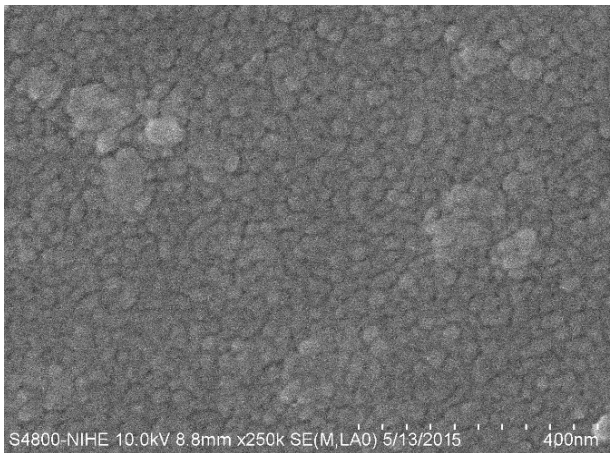

Figure 2. SEM image of $BaSnO_3$ powders film obtaining by doctor – blade method. The powders were cacilned at 623 K – 5h and the film was thermal annealing at 150ºC – 1 h. The scale bar is 400 nm.

3.2. Optical Energy Gap Determination

The UV-vis absorption spectra of the calcined thin film at 623K are illustrated in Figure. 3. The absorption spectra exhibit a strong absorption band with a steep edge at less than 360 nm and a broad band with very weak intensity in visible region. This strong absorption band can be attributed by band-to-band transitions which correspond to the 2p(O) to 5s(Sn) states [20, 21].

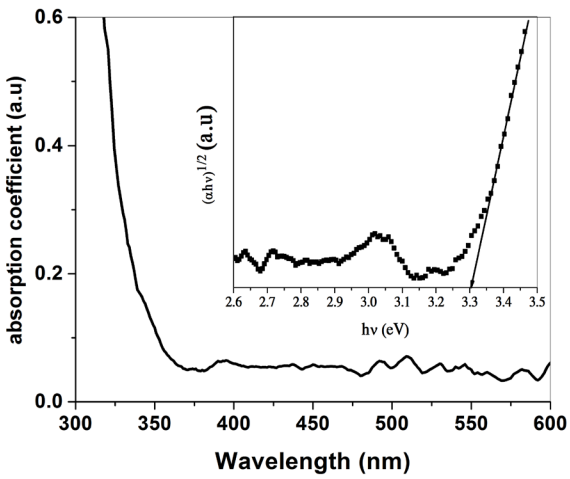

Figure 3. The absorption spectra of $BaSnO_3$ film of calcined $BaSnO_3$ at 623 K – 5h. Inset is absorption curve plotting the $(\alpha h\upsilon)^{1/2}$ versus hυ

The relation between the absorption coefficient (α) and the incident photon energy (hν) can be determined by using Tauc's relationship in the high absorption region of semiconductor, as follows [16, 17, 24]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (2)$$

where A is a constant and sometimes called the band tailing parameter and it is an energy independent constant, E_g is the optical energy gap, which situated between the localized states near the mobility edges. n is the power factor of the transition mode. The values of (n) for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions are n = 1/2, 2, 3/2 and 3, respectively [16, 17, 24]. In this case, $BaSnO_3$ is a semiconductor with an indirect the band gap and suitable with n = 2. In order to determine the optical energy gap, we plot $(\alpha h\nu)^{1/2}$ versus the photon energy (hν), which is shown in inset of Figure 3. It reveals that the obtained plotting gives a straight line in a certain region, one can extend this straight line to intercept (hν)-axis at $(\alpha h\nu)^{1/2} = 0$. The estimated value of the energy gap was about 3.31 eV and consisted with experimental values of indirect band gap from 3.1 to 3.4 eV [18, 22, 23].

3.3. Luminescence and Excitation Characteristics

Photoluminescence and excitation spectra of calcined samples at different temperatures are shown in Figure 4 and Figure 5, respectively. The luminescence spectra in Figure 4 were broad radiative bands from 400 to 600 nm with peak centered at around 460 nm.

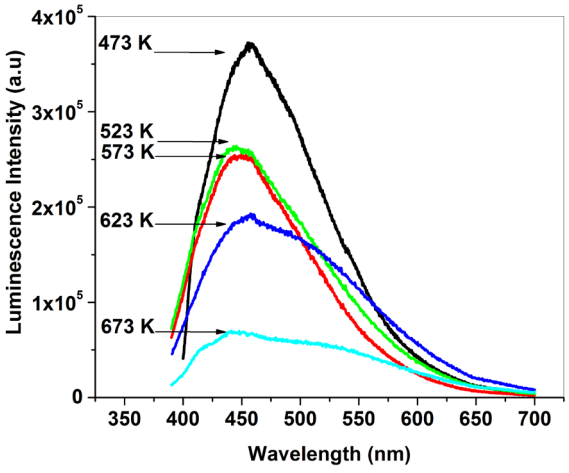

Figure 4. Photoluminescence spectra of $BaSnO_3$ with different calcined temperatures from 473 K up to 673 K, λ_{exc} = 370 nm

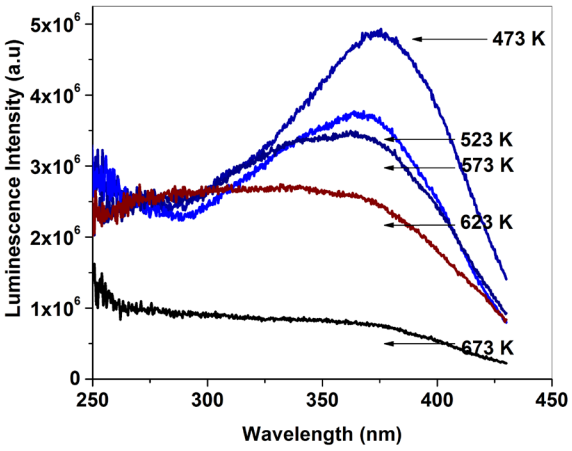

Figure 5. Excitation spectra of calcined $BaSnO_3$ at different temperature from 473 K up to 673 K, monitored radiative at 460 nm

In both of luminescence and excitation spectra, the emission decreased with increasing temperature of thermal annealing process. In this case, the radiative are probably relative to the emissions of defect centers and the decreasing of luminescence intensity of samples due to decreasing of defects in host [15, 20, 21]. As discussion in XRD measurement, the phase structures of materials were transformed after the heat treatment at 573 K, in which the forming of $BaSnO_3$ crystallites due to the removal of a large amount of hydroxyl groups from $BaSn(OH)_6$ complexes during calcination. Moreover, the crystallization process of $BaSnO_3$ will reduces not only hydroxyl groups but also O-related defects such as non-bridging oxygen, vacancy oxygen [15, 20, 21] and this process also makes the crystallite structures to be becoming more complete.

4. Conclusions

Perovskite $BaSnO_3$ powder and thin film have been successfully synthetized by hydrothermal condition with different annealed temperature from 423 to 673 K for 5 h. The samples are uniform particles with average size around 40 - 42 nm. The $BaSnO_3$ crystallites were formed after thermal annealed process and their energy ban gap is about 3.31 eV. Moreover, the thermal annealing process has made also crystallite structure more complete through the reducing of hydroxyl groups and defects in host. The high optical transparent in visible region of this material thin films well meet the requirement of photo-anodes for DSSCs applications.

Acknowledgements

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