http://dx.doi.org/10.5012/bkcs.2014.35.6.1887

A Facile Synthesis and Characterization of Sodium Bismuth Sulfide ($NaBiS_2$) under Hydrothermal Condition

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Received January 14, 2014, Accepted February 25, 2014

Key Words : Sodium bismuth sulfide, Hydrothermal reaction, L-Cysteine, X-ray diffraction, Band gap

Binary bismuth chalcogenides have received considerable attention for their application in thermoelectric materials; however, there have been relatively fewer reports on the ternary and quarternary bismuth chalcogenides; but nevertheless, a slowly growing number of them can be found.[1] Among them, NaCl-type $MBiQ_2$ (M = Li, Na, K; Q = S, Se) is the most elementary, and was first synthesized 70 years ago in a solid state reaction, and the structures of them have been determined merely by the powder X-ray diffraction method (XRD).[2-5] Synthetic methods had been largely limited to molten salt synthesis in a sealed quartz tube for very long reaction time (~9 d)[5], until Qian *et al.* reported that $NaBiS_2$ could be isolated as a byproduct, during the synthesis of 1-D bismuth sulfide (Bi_2S_3) nanoribbons, under solvothermal condition (glycerol:water = 2:1).[6,7] In that report, when higher concentration of NaOH is added to the reaction medium, $NaBiS_2$ is found at the bottom of the autoclave.[6] The $NaBiS_2$ was characterized only by XRD and scanning electron microscopy (SEM), but no other characterization was performed.[6] Inspired by this finding, we have tried to synthesize sodium bismuth sulfide as a sole product, in aqueous medium. Herein, we report the synthesis of $NaBiS_2$ as the sole product by hydrothermal reaction, for the first time. The synthesis produced $NaBiS_2$ nanosheets, and it was characterized by XRD, diffuse reflectance spectrophotometry, X-ray photoelectron spectroscopy (XPS), and elemental analysis by energy dispersive X-ray spectroscopy (EDX). This synthetic method might open up new opportunities to access $NaBiS_2$, and is environmentally benign; it might therefore be utilized in a variety of fields, including thermoelectric materials, and light harvesting materials.

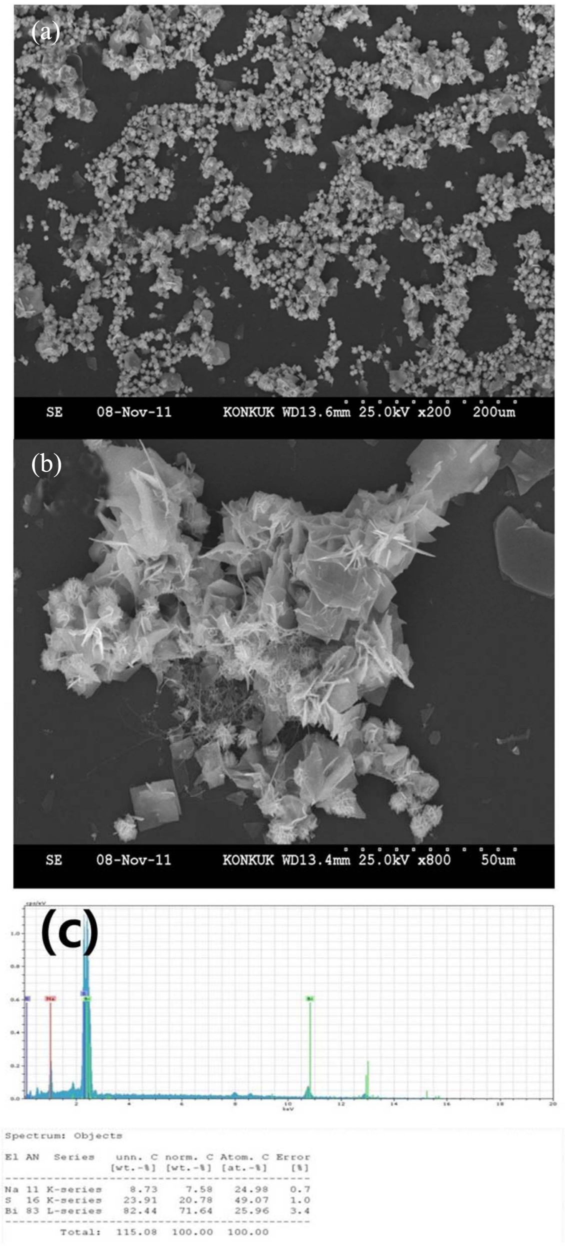
Experimental Section

All the chemicals were of analytical grade, and were used as-received, without further purification. Distilled water was purified by a New P.nix UP 900 water purification system (Human Corporation, South Korea). IR spectra were recorded, using a MIDAC M series spectrometer. Powder X-ray diffraction (XRD) data were collected at 40 kV and 35 mA, using a Philips X'pert MPD diffractometer (Philips Analytical, Netherlands); CuK_α radiation was used as the source (λ = 1.5418 Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were performed, using a Bruker Quantax 200 125ev SEM spectrometer (Germany). X-ray photoelectron spectra (XPS) were recorded, using an ESCALAB 210 X-ray Photoelectron Spectroscope.

Synthesis of Sodium Bismuth Sulfide. Synthesis of sodium bismuth sulfide ($NaBiS_2$) was performed by the following procedures: $Bi(NO_3)_3\cdot 5H_2O$ (40 mM, 4.0 mmol) and L-Cys (120 mM, 12.0 mmol) were mixed to make a 100 mL of aqueous solution, followed by adding NaOH (2.5 M, 0.25 mol). The resulting solution was transferred to a teflon-lined autoclave reactor, and stirred with magnetic stirrer for an additional 30 min. Subsequently, the autoclave reactor was placed in an electric convection oven, with the pre-heated temperature at 180 °C for 72 h. After the reaction was completed, the reactor was cooled to room temperature. The resulting solid product was washed with ethanol and isopropyl alcohol several times with centrifugation (3000 rpm), and dried in a vacuum overnight, to give pure product as black powder (yield = 46%).

Results and Discussion

We investigated the synthesis and characterization of sodium bismuth sulfide ($NaBiS_2$) under a hydrothermal condition, from a solution containing bismuth nitrate as a bismuth ion source, L-cysteine (L-Cys) as a sulfur source, and excess amount of NaOH, to push the reaction to produce the $NaBiS_2$. For this purpose, the concentration of NaOH was adjusted at the saturation level; otherwise, Bi_2S_3 would have been generated as an impurity. L-Cys has been used as a sulfur source (S^{2-}) in synthesizing sulfur-containing materials, in many other reports.[8] The isolated product was black powders, and shows an instability towards water. This instability toward water may originate from the structure, in which S^{2-} ions occupy the Cl^- site, and Na^+ and Bi^{3+} occupy the Na^+ site, in the NaCl structure. Na^+ ions are washed out of the structure in water; therefore, it is desirable to wash with ethanol and isopropyl alcohol. Figures 1(a) and 1(b) show the morphologies of the product. Particles of the product are largely tens of micrometers in size; they are composed of thin 2-D plates entangled with each other. The thickness of the 2-D plates is in the range of ~200 nm. Elemental analysis was performed, using energy dispersive X-ray analysis (EDX). The result reveals that the Na/Bi/S



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Spectrum: Objects

El AN   Series    unn. C norm. C Atom. C Error
                  [wt.-%] [wt.-%] [at.-%]   [%]
-----------------------------------------------
Na 11 K-series    8.73     7.58   24.98   0.7
S  16 K-series   23.91    20.78   49.07   1.0
Bi 83 L-series   82.44    71.64   25.96   3.4
-----------------------------------------------
        Total:  115.08   100.00  100.00
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Figure 1. (a) and (b) SEM images, and (c) EDX spectrum of $NaBiS_2$.

ratio obtained in the product was 24.98:25.96:49.07, which is close to 1:1:2 ratio (Fig. 1(c)), which shows the purity of the sample.

In order to elucidate the structure of the product, we performed powder X-ray diffraction (XRD) experiments. As can be seen in Figure 2, the XRD pattern suggests that it matches with NaCl-type $NaBiS_2$ (Fm-3m No. 225), and it proved to be that of sodium bismuth sulfide ($NaBiS_2$) (ICCD No. 01-075-0065). The cell dimension determined by Rietveld analysis is $a = 5.76$ Å with X'pert Highscore Plus.[9] No peak, other than those of $NaBiS_2$, was found, which also indicates the purity of the product. XRD, as well as EDX data, support that the obtained product is highly pure. In addition, from the XRD pattern, we could determine the crystallite size of the product.[11] Even though the apparent morphology of the product (entangled 2-D sheet) is tens of micrometers in size, it could consist of small crystals, and could therefore be nanocrystalline. The crystallite size of the product was determined by the Debye-Scherrer equation:[10]

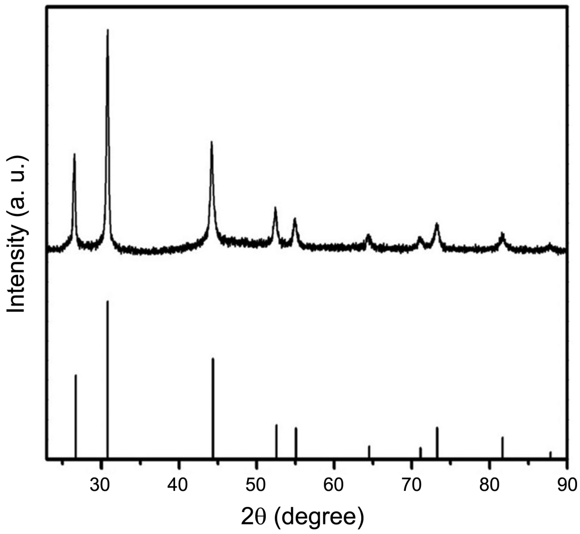

Figure 2. XRD pattern of $NaBiS_2$ (top), and peak assignment by ICCD No. 01-075-0065.

$$D = 0.9\,\lambda / B\cos\theta$$

where, D is the coherence length of the crystallite; λ is the wavelength of the light source; B is the full-width at half maximum (FWHM) of the peak; and θ, the angle of diffraction. The calculated coherence length of the crystallite is approximately 14 nm, which indicates that the product is highly crystalline, and nano-sized.

To investigate the electronic properties of the product, diffuse-reflectance UV-vis spectrophotometry was performed, to estimate the forbidden band gap energy (E_g) of the product. The E_g of the product was found to be approximately 1.4 eV, as shown in Figure 3. Gabrel'yan *et al.* reported the calculated band gap energy of $NaBiS_2$ to be

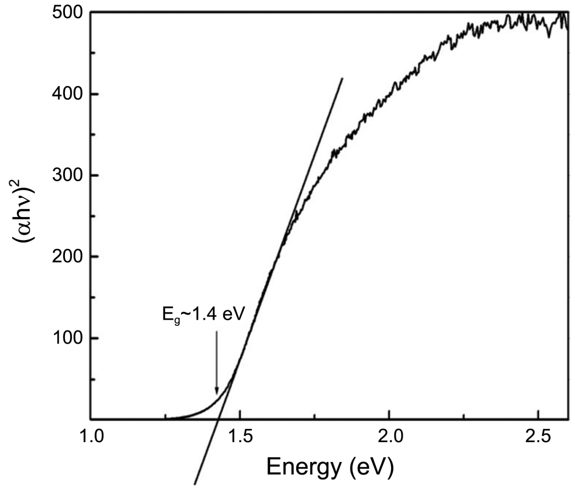

Figure 3. Diffuse-reflectance UV-vis spectrum of $NaBiS_2$.

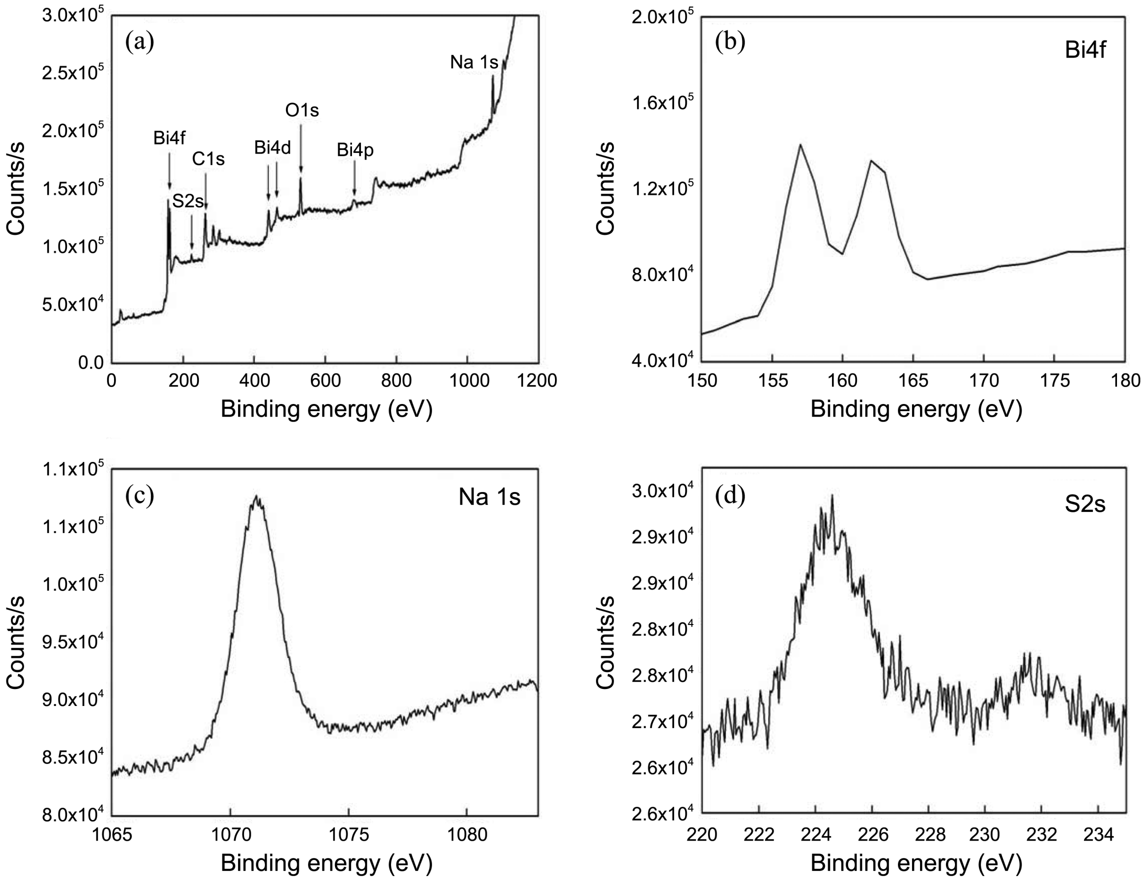

Figure 4. XPS spectra of (a) full span, (b) Bi4f, (c) S2s, and (d) Na1s of $NaBiS_2$.

1.28 eV, which was based on the experimental lattice parameter (ELP).[11] The ELP method utilizes the cell parameters as input data to calculate the E_g. Surprisingly, the obtained E_g is the largest one ever estimated for $NaBiS_2$, indicating the nanocryatalline nature of $NaBiS_2$. Usually, solid state materials undergo broadening of E_g, upon decrease in crystallite sizes. This corresponds to the E_g of bismuth sulfide (Bi_2S_3), which may be utilized as semiconducting and thermoelectric materials. Furthermore, materials with a low band gap (< 1.8 eV) have been intensively reported, because they could be utilized as light harvesting materials.[12] Therefore, the product ($NaBiS_2$) could also potentially be applied to hybrid solar cell applications.

XPS was used to evaluate the composition and purity of the sample. XPS spectroscopic analysis shows that all the peaks coming from the elements comprising $NaBiS_2$ were observed, as shown in Figure 4. The peaks corresponding to O and C in Figure 4(a) are known to originate from O_2, H_2O, and CO_2 adsorbed on the surface of $NaBiS_2$ plates in the air.[13] Figures 4(b)-(d) show narrow-scanned photoelectron spectra of Bi4f, S2s, and Na1s, respectively.

Conclusions

We have synthesized $NaBiS_2$ as the sole product by hydrothermal reaction, for the first time. $NaBiS_2$ was found to be pure in composition and structure, and is nanocrystalline by SEM, and by XRD and XPS techniques. The product was further characterized by diffuse-reflectance UV-vis spectrophotometry, to be a low band gap material. This facile synthetic method might open up new opportunities to access $NaBiS_2$, and is environmentally benign; it may therefore be utilized in a variety of fields, including thermoelectric materials, and as a material for hybrid solar cell applications.

Acknowledgments. This research was supported by the National Research Foundation (NRF) funded by the Ministry of Education, Science and Technology (Grant No. 2010-0024851).

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