Microwave-assisted synthesis of nanosized Bi_2Se_3

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The polyol method was applied to the microwave synthesis of nanostructured Bi_2Se_3. Nanosized Bi particles were obtained as an intermediate in this reaction. The product was characterized by XRD, EDAX, and TEM measurements. The corresponding reaction with tellurium did not yield Bi_2Te_3. Instead $Bi_3Te_4$is obtained.

Introduction

In recent years there has been considerable interest in semiconductors of nanometer dimensions due to the quantum size effect that they exhibit.[1–3] Semiconductor selenides have already found applications as sensors, laser materials, optical filters, solar cells, and many other devices.[4–6] Bi_2Se_3 has attracted much attention due to its applicability in electromechanical devices,[7] optical recording system,[8] strain gauges,[9] thermoelectrical devices,[10–12] narrow gap semiconductors (E_{gap} = 0.25 eV)[13] and also because of its very anisotropic layered structure.

In the last few years new methods for the synthesis of Bi_2Se_3 have been developed. Wang *et al.* have reported about a novel solvothermal method at low temperatures. The solvothermal process used $BiCl_3$, Se, and NaI, which were heated in an autoclave at 130 °C for 4 h.[14] In another publication, Desai *et al.* described the galvanostatic electrodeposition of Bi_2Se_3 thin films that were prepared from an aqueous alkaline bath using sodium selenosulfite (Na_2SeSO_3) as a selenide ion source and triethanalomine (TEA) as a complexing agent.[15]

The synthetic route of Giani *et al.* for fabrication of Bi_2Se_3 thin films used a metalorganic compound, decomposing it *via* the chemical vapor deposition (MOCVD) technique. Trimethylbismuth (TMBI) and diethylselenium (DESe) were employed as the metalorganic sources. The MOCVD of Bi_2Se_3 was carried out in a horizontal reactor over a temperature range varying from 450 °C to 500 °C, and under a hydrogen flow.[16] In all cases, very prolonged heating time was needed to obtain the desired product.

Recently, we have found that the application of microwave radiation greatly facilitates the use of the polyol method for the preparation of binary chalcogenides.[17] In most experiments, the microwave reaction is completed within a few minutes, the maximum duration being one hour.

The application of microwaves in inorganic chemistry began only in the late 1980s.[18] Ethylene glycol (as well as other glycols) is an excellent susceptor of microwave radiation because of its high permanent dipole. This is important because in the polyol reaction ethylene glycol serves as a reducing agent only at high temperatures. In the polyol reaction metallic nanoparticles are produced as intermediates, resulting from the reduction of their ions. These metallic particles are also good susceptors of microwave radiation, which causes rapid heating of these metallic nanoparticles. They will heat up, while the temperature of their surrounding will be close to the boiling point of the solvent. This leads to a situation in which the local temperature around the metallic nanoparticles will be much higher than that of surrounding liquid. Whittaker and Mingos[19] recently reported that high boiling point alcohols are superior solvents in microwave-assisted reactions because they help prevent arcing, which is known to lead to the decomposition of solvents, resulting in carbon and carbonaceous residues. Arcing is considered the main source of the high level of impurities, which are found in the end product.

In this article, we report on the synthesis of Bi_2Se_3 nanocrystals which have been prepared by the microwave-assisted polyol method. In this simple and quick reaction, the polyol (ethylene glycol) is both the solvent and the reducing agent. Although the polyol method has already been applied to a few divalent metallic ions,[17] it is hereby extended to a trivalent ion, Bi^{3+}. This extension demonstrates that the only criterion by which the polyol reaction is governed is the reduction potential of the metallic ion.

Experimental

All reagents were of the highest commercially available purity. Elemental Se, bismuth oxynitrate, $BiONO_3$, and ethylene glycol were purchased from Aldrich Co. and used without further purification. The X-ray diffraction patterns of the products were recorded with a Bruker AXS D8 Advance Powder X-ray Diffractometer (using CuKα λ = 1.5418 Å radiation). Peak fitting and lattice parameter refinement were computed using the Topas and Metric programs (Bruker Analytical X-Ray Systems). EDS measurements were done on an X-ray microanalyzer (Oxford scientific) built on a JSM-840 Scanning Electron Microscope (JEOL). The transmission electron micrographs (TEM) were imaged on a JEOL-JEM 100SX microscope, using a 100 kV accelerating voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, electron microscopy sciences) coated with carbon film. The grid was then air-dried.

The microwave-assisted reaction was carried out in a Spectra-900 W microwave oven, with a 2.45 GHz working frequency. The oven was modified to include a refluxing system. In all experiments, the microwave oven was cycled as follows: on for 21 s, off for 9 s, with total power always at 900 W. This cycling mode was chosen in order to reduce the risk of superheating the solvent. All reactions were conducted under the flow of nitrogen.

Microwave synthesis

The dissolution of bismuthoxynitrate in ethylene glycol was assisted by the addition of NaOH, and by its gentle heating

in the microwave oven for approximately 1 minute. Stoichiometric quantities of Se powder were then added (Bi:Se = 2:3). The system was purged for a few minutes with nitrogen prior to the turning on of the microwave reactor. The reactions were conducted for 30 min under nitrogen. In the post-reaction treatment, the product was centrifuged once with the mother liquid, and a few times with ethanol, at 20 °C and 9000 rpm. The product was then dried overnight under vacuum.

Results and discussion

XRD study: The as-prepared material was characterized by X-ray powder diffraction, which showed (Fig. 1**a**) a perfect match with the diffraction pattern of Bi_2Se_3, as published in the literature. (PDF # 33-0214). The average Bi_2Se_3 size was determined from the diffraction patterns by using the Debye–Scherrer (DS) equation.[20] The particle size was found to be 20 nm. All of the diffraction patterns were attributed to Bi_2Se_3, and no diffractions assigned to impurities were found.

Even the intensity ratios of the diffraction peaks were in accordance with the literature. A one phase diffraction pattern is obtained when the reaction is carried out for 30 minutes. Smaller particles (20 nm according to the DS calculation) were obtained for the shorter irradiation time. If the reaction is conducted for 1 hour, however, some additional weak diffraction peaks are observed. They are assigned to Bi_3Se_4. Fig. 1b illustrates these additional diffraction peaks.

TEM measurements: The TEM picture of the as-prepared product is demonstrated in Fig. 2. Cucumber-like shapes

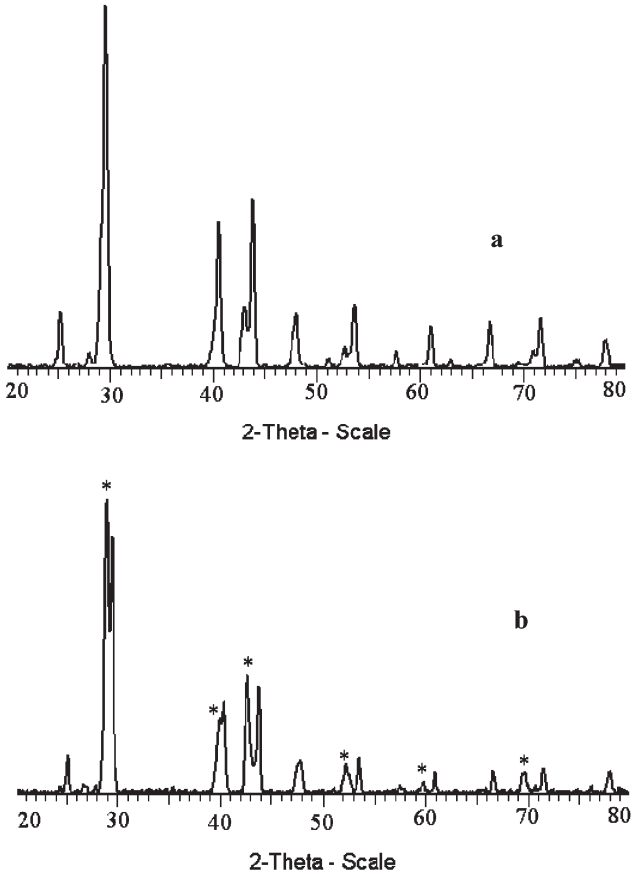

Fig. 1 XRD pattern of (a) the as-prepared after 30 min single phase Bi_2Se_3, and (b) the sample containing two phases *i.e.* Bi_2Se_3, and Bi_3Se_4 after 1 h (* marks indicates Bi_3Se_4 phase).

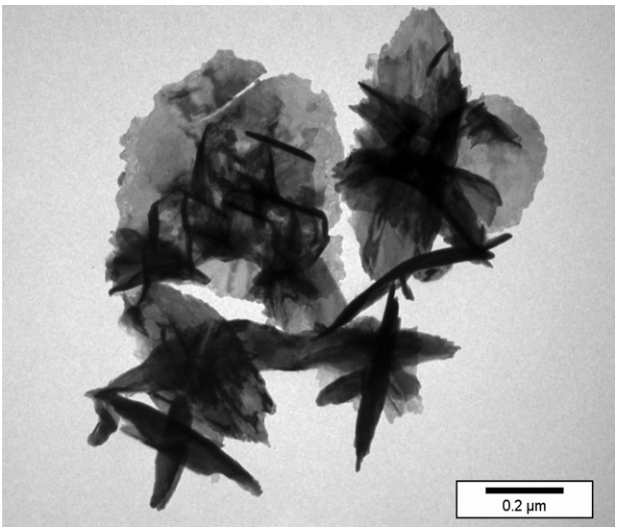

Fig. 2 TEM image of the as-prepared Bi_2Se_3.

whose length is about 300 nm and width 20–80 nm, are observed as the preferred structure of the individual particles. It seems that these structures tend to agglomerate, forming planar, leaf-like aggregates. A comparison of the TEM data with the XRD results leads us to conclude that the basic particles of 20 nm in size (according to the XRD) are smaller than those observed in the TEM picture. The TEM picture represents various modes of aggregation.

EDX measurements: The stoichiometric ratio between the elements comprising the as-prepared products was obtained from EDX measurements. We have found the atomic ratio of Bi:Se to be 39.7:60.3. The composition of the resulting solid is identical to the initial ratio of the constituent elements introduced in the solution. This indicates that materials are not lost during the microwave irradiation.

Proposed mechanism

The formation of Bi_2Se_3 by microwave irradiation is based on the observation that in microwave boiled solvents, the solvents themselves can undergo profound overheating.[21–24] As a result of such overheating, the metal ion could be reduced to the metal in the zero oxidation state. Such metallic particles may strongly interact with microwave radiation, yielding very high temperatures, which will enhance the reduction of selenium atom.

In order to succeed in obtaining the metallic particles, the reagents must be soluble in ethylene glycol and independently reducible by the solvent.[25] The bismuthoxynitrate is soluble in ethylene glycol and is reduced to bismuth in its zero oxidation state.

It is well known, that the reduction potential of Bi^{3+} is 0.308 V. ($Bi^{3+} + 3\ e^- \leftrightarrow Bi^0$ 0.308 V). This low reduction potential makes it easy to reduce Bi^{3+} to Bi^0. To check this hypothesis, we conducted a microwave reaction in the absence of Se. Bismuthoxynitrate was dissolved in ethylene glycol by adding NaOH, and the mixture was gently heated in the microwave oven for 1 minute. After this stage, the system was purged for a few minutes with nitrogen prior to turning on the microwave reactor for 1 h. Metallic Bi^0 (Fig. 3) was obtained at the end of the reaction as evidenced by the XRD measurement. On the other hand, unlike the Bi^{3+}, Zn^{2+} ions could not be reduced to metallic Zn under the same conditions. We attribute this failure to the reduction potential of Zn^{2+} being −0.7618 V ($Zn^{2+} + 2e^- \leftrightarrow Zn^0$). We have also tried to apply the same method for the synthesis of Bi_2Te_3. However, instead of Bi_2Te_3, we have obtained Bi_3Te_4. The synthesis and details of this reaction

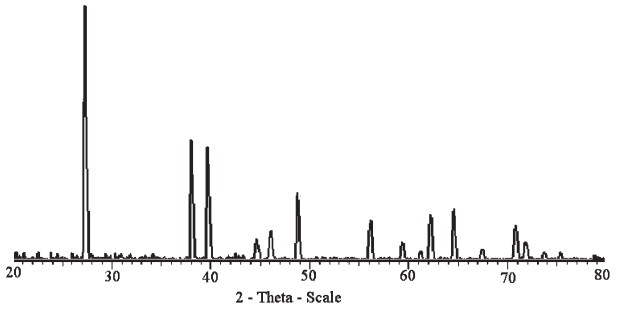

Fig. 3 XRD pattern of as-prepared metallic Bi^0.

will be described elsewhere. The tellurium reaction was amenable to experimental observation because the reduction potential of Se and Te are close to each other. The reduction potential of these two chalcogenides are $Se + 2e^- \leftrightarrow Se^{2-}$ $E^0 = -0.924$ V; $Te + 2e^- \leftrightarrow Te^{2-}$ $E^0 = -1.143$ V. The heated bismuth, at the boiling temperature of ethylene glycol, cannot reduce the tellurium, while it can reduce the Se because of a lower reduction potential. The reaction has also been conducted by introducing the relative concentrations of metallic Bi, and Se in ethylene glycol. Bi_2Se_3 is indeed obtained under these conditions, however, a great excess of unreacted Se is detected. The EDAX results of the as-prepared mixture shows a composition of 23.23 atomic percent Bi, and 76.77 atomic percent Se. This indicates that the *in situ* prepared nanosized Bi is heated to a much higher temperature enabling the reduction of the Se atoms. Further studies on the dependence of other polyols on the reduction power of the metallic nanopowders obtained in a microwave reaction are in progress. Further experimentation with higher polyols is under progress.

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