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Preparation and Characterization of Nanomaterials of Tellurium, Bismuth, and Bismuth Telluride

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In order to improve the processing and performance of tellurium (Te), bismuth (Bi), and bismuth telluride (dibismuth tritelluride, Bi_2Te_3), which are valuable thermoelectric materials that operate near room temperature in the bulk state, a nanometer scale synthetic method, in which the starting materials are reduced with $NaBH_4$ in the presence of protecting agents in solution under mild conditions, was used. Te nanorods having an average diameter of 10 ± 3 nm (aspect ratio = 3.0) were prepared by reducing tellurium(IV) ethoxide in ethanol in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) under nitrogen. Although Bi nanoparticles prepared from bismuth(III) chloride by this method have an average diameter of 29 ± 8 nm, PVP-protected Bi_2Te_3 nanoparticles have a really small average diameter (7 ± 5 nm) and they are probably the smallest Bi_2Te_3 particles ever reported. Heat treatment of PVP-protected Bi_2Te_3 nanoparticles in refluxing solvents was found to improve the stability.

Heat energy, generally produced by combustion of fossil fuels, is commonly used in human society because of the high density of energy. However, the waste heat energy exhausted from automobiles and electric power stations as well as natural heat energy cannot be effectively utilized because of the low density of energy. Effective and economical utilization of these low density energies is needed to resolve the energy problems for human beings.

Recently, much attention has been paid to the direct conversion of heat energy to electric energy by using thermoelectric materials. The proposed thermoelectric materials are usually inorganic semiconductors.[1–9] Among them bismuth telluride (dibismuth tritelluride, Bi_2Te_3) is a thermoelectric material that works effectively in a relatively low temperature region from room temperature to ca. 250 °C. In addition, the thermoelectric property of Bi_2Te_3 can be controlled as both p-type and n-type characteristics depending on the chemical composition.[10–12] Since these materials have a thermoelectric figure-of-merit, *ZT*, of ca. 1.0, devices containing both p- and n-type materials have been already used in practical thermoelectric refrigeration, for example. However, the conventional method for preparation of Bi_2Te_3 materials is based on co-sintering of the corresponding metal elements at elevated temperatures under special conditions, and the devices are fabricated via various manufacturing processes like etching and polishing.[13] Such severe reaction conditions and fine manufacturing processes result in high cost for these thermoelectric devices, which is a disadvantage of the conventional bulk materials.

Thus, nanomaterials have received much attention. Nanomaterials or nanoparticles are expected to improve the processability, because the structure of materials can be modified at rather low temperature by taking advantage of the low melting point of nanoparticles, and devices with various shapes can be directly made by utilizing a template during the preparation process without mechanical manufacturing processes.[14] In addition, Venkatasubramanian et al. reported that superlattice structured films composed of alternatively layered Bi_2Te_3 and Sb_2Te_3 on the order of a few nanometers show thermoelectric performance twice as high as the bulk alloy materials.[15] Chen and Shakouri estimated that quantum size effects can improve the thermoelectric properties of materials by controlling the structure two- or three-dimentionally.[16] Recently, Zhou et al. reported that Bi_2Te_3 nanowires of 50–100 nm in diameter, prepared by electrodepositions, had a Seebeck coefficient (*S*) 15–60% larger than the bulk ones at 300 K.[17] Thus, Bi_2Te_3 nanomaterials on the order of a single nanometer should have a much larger Seebeck coefficient than the bulk ones.

However, there are only few reports of the preparation of nano-scaled Bi_2Te_3 materials by chemical methods, which have advantages for mass production compared to physical methods. Yu et al. reported the preparation of the Bi_2Te_3 nanowires by the reaction of $BiPh_3$ with Te nanowires, which were prepared in advance by the decomposition of $TeCl_4$ in the presence of trioctylphosphine oxide (TOPO) in a polydecene solution at 573 K.[18] These nanowires are uniform, but have a large mean diameter (68 ± 17 nm) and a length of several micrometers. In contrast, Deng et al. reported Bi_2Te_3 nanoparticles[19] prepared by the solvothermal reaction of $BiCl_3$ and metallic Te powder using KBH_4 in a Teflon autoclave.[20,21] In this method, the Bi_2Te_3 nanomaterials were not uniform and had various shapes, such as particles, rods, and square-plates, and various sizes from 20 to 600 nm, which depended on the reaction temperature and time.[20] By addition of protecting agents, such as disodium ethylenediaminetetraacetate, into the reaction system, Bi_2Te_3 nanomaterials changed morphology, e.g., they became a sheet-rod, but still had a large size (about 100–200 nm).[21] All of these nanomaterials often aggregated in and precipitated from solution, and were difficult to control the size. Therefore, a new preparation method for Bi_2Te_3 nanomaterials on the order of a single nanometer in size for

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improvement of thermoelectric properties and processability is needed.

Here, we report the simple syntheses of well-dispersed nanomaterials of Te, Bi, and Bi_2Te_3 on the order of a single nanometer in size by $NaBH_4$ reduction using poly(*N*-vinyl-2-pyrrolidone) (PVP) or trioctylphosphine oxide (TOPO) as protecting agents under nitrogen.

Experimental

Chemicals. Bismuth(III) chloride ($BiCl_3$), sodium tetrahydroborate ($NaBH_4$), poly(*N*-vinyl-2-pyrrolidone) (PVP, K30, MW = 40000), and trioctylphosphine oxide (TOPO) were purchased from Wako Chem. Ind. Ltd., and used as received. Tellurium(IV) ethoxide ($Te(OC_2H_5)_4$) was purchased from Azmax Co. and used as received. Ethanol was treated by bubbling with purified nitrogen (99.999%) for 3 h in advance to remove dissolved oxygen.

Preparation of Protected Tellurium Nanomaterials. During the reaction and purification processes, the complete omission of contaminating oxygen from nitrogen atmosphere was very important. Thus, all of the reactions and purification processes presented in this manuscript were carried out in a dry box filled with purified nitrogen. A typical experiment was carried out as follows: $Te(OC_2H_5)_4$ (12.0 mg, 0.033 mmol) and PVP (147 mg, 1.32 mmol in monomer unit) or TOPO (510 mg, 1.32 mmol) were each completely dissolved in 10 cm^3 ethanol. The two solutions were mixed in a two-neck flask under nitrogen, and the mixture was stirred for 3 h after addition of 20 cm^3 degassed ethanol. To the mixed solution (40 cm^3), which had been cooled down to 273 K with an ice bath, 10 cm^3 of ethanol solution of $NaBH_4$ (20.0 mg, 0.53 mmol) was added dropwise over 10 min from a dropping funnel. After allowing the temperature to increase from 273 K to room temperature over a few hours while stirring, the mixture was heated up to the boiling point with an oil bath and refluxed for 5 min. After cooling the mixture to room temperature while stirring, the obtained brownish black mixture was subjected to ultrafiltration (Advantec Co., Ltd., Ultrafilter Q0100) and wash 3 times with degassed ethanol under a pressure of nitrogen to remove any remaining ionic species. The solvent was removed with a rotary evaporator. The residue was dried at 353 K under vacuum overnight to form black powder, which was kept under nitrogen for characterization.

Preparation of Protected Bismuth Nanoparticles. The same procedures as the case of Te nanomaterials were applied to the preparation of PVP- or TOPO-protected Bi nanoparticles, but using $BiCl_3$ (10.4 mg, 0.033 mmol) instead of $Te(OC_2H_5)_4$. The obtained powder was brownish black.

Preparation of Protected Bismuth Telluride. $BiCl_3$ (4.2 mg, 0.013 mmol), $Te(OC_2H_5)_4$ (7.2 mg, 0.020 mmol), and PVP (147 mg, 1.32 mmol in monomer unit) were each separately dissolved in 10 cm^3 ethanol. The $BiCl_3$ and $Te(OC_2H_5)_4$ solutions were mixed in a two-neck flask, and the mixture was stirred for 1 h. To this mixture was added 10 cm^3 solution of PVP or TOPO in ethanol. The mixture was stirred for 3 h or more in a two-neck flask after the addition of 20 cm^3 degassed ethanol. The mixture was cooled to 273 K with an ice bath, and a 10 cm^3 of ethanol solution of $NaBH_4$ (20.0 mg, 0.53 mmol) was added dropwise over 10 min. The resulting mixture was heated to boiling point with an oil bath and then allowed to reflux for 1 h. Because the heat treatment was designed to be carried out at temperatures higher than the boiling point of ethanol, 50 cm^3 of ethylene glycol was added to the residue after the ethanol was evaporated from the mixtures, and the ethylene glycol solution was heated at the boiling point for additional 1 h. The black mixture was purified by ultrafiltration, evaporation, and drying to give black powders by the method similar to the case of protected Te nanomaterials.

Characterization. Transmission electron microscopic (TEM) measurements were carried out using a JEOL JEM-1230 electron microscope operated at 80 kV. The average sizes in diameter (d_{av}) and size distribution histograms of the nanoparticles were calculated by counting ca. 200 particles from the TEM micrograph. The standard deviation (σ) of nanoparticles were calculated by assumption of normal distribution. The X-ray diffraction patterns were obtained by using a Mac Science Co. M18XHF-SRA diffractometer with Cu Kα radiation ($\lambda = 0.154187$ nm) for the powder samples at room temperature. The crystalline sizes of the samples were calculated by Scherrer's equation ($D = K \cdot \lambda / \beta \cos\theta$) using $K = 0.94$ without correction due to the apparatus.[22] The particle composition was determined with an energy dispersive X-ray analyzer (EDX) attached to a JEOL JEM-1230 electron microscope. An atomic emission spectroscopy using an inductively coupled plasma (ICP) as the excitation source (Shimadzu ICPS-7500) was also used for elemental analysis of the nanomaterials.

Results and Discussion

Synthesis of Tellurium Nanorods. In order to develop a homogeneous system for the synthesis of Te nanomaterials with uniform size and shape, we used $Te(OC_2H_5)_4$, which is commercially available and easily soluble in ethanol, as the source of Te. When $Te(OC_2H_5)_4$ in solution was reduced with $NaBH_4$ in the presence of PVP in ethanol at 273 K and the solution heated to reflux for a while under nitrogen, the colloidal dispersions of Te nanorods were obtained.

When $NaBH_4$ was added into an ethanol solution of $Te(OC_2H_5)_4$ in the presence of PVP at room temperature, the color of the solution changed to brownish black, indicating the reduction of the Te^{IV} ions to form the Te nanomaterials. In order to confirm the formation of nanomaterials, transmission electron microscopy (TEM) was used. In the beginning of experiments, we could observe the nanomaterials by TEM operated under low voltage and low current density, but failed to acquire TEM photographs of the Te nanomaterials by operating TEM under enough voltage and current density to take the photograph. It is probably because the small Te nanomaterials have a low melting point and, possibly, they may have an amorphous structure. Thus, we successively heated at the mixture at reflux in order to obtain large crystals. In TEM photograph of Te nanomaterials obtained by successive heat treatment in the presence of PVP (Fig. 1a), nanorods with considerably uniform size and shape, ($d_{av} = 10 \pm 3$ nm and average length of 30 ± 9 nm (average aspect ratio of 3.0)) were obtained. If the reaction was carried out with TOPO as the protecting agent instead of PVP, the nanorods (Fig. 1b) were neither small nor uniform ($d_{av} = 24 \pm 7$ nm, average aspect ratio = 4.4) as those using PVP.[23] Without any protecting agent, in contrast, the same reaction resulted in large particles that were more than a few micrometers in size as shown in Fig. 1c.

These results have demonstrated that heat treatment in refluxing ethanol is very important for the synthesis of stable Te nanorods and that PVP is a very effective protecting agent in comparison with TOPO for Te nanomaterial synthesis. Both PVP and TOPO are considered to coordinate to Te^{IV} ions

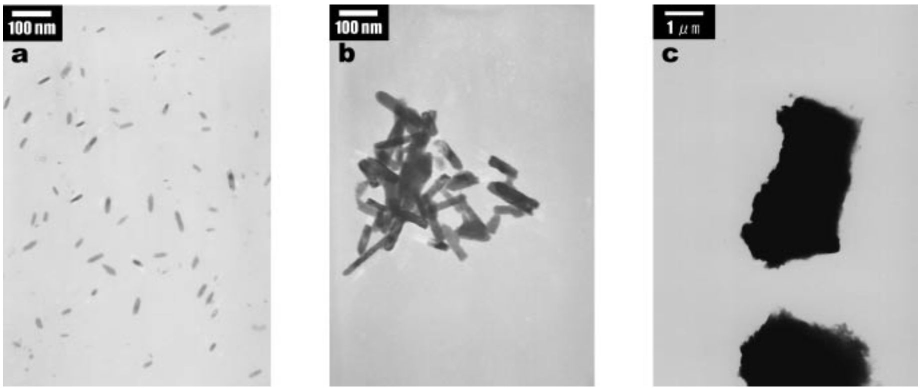
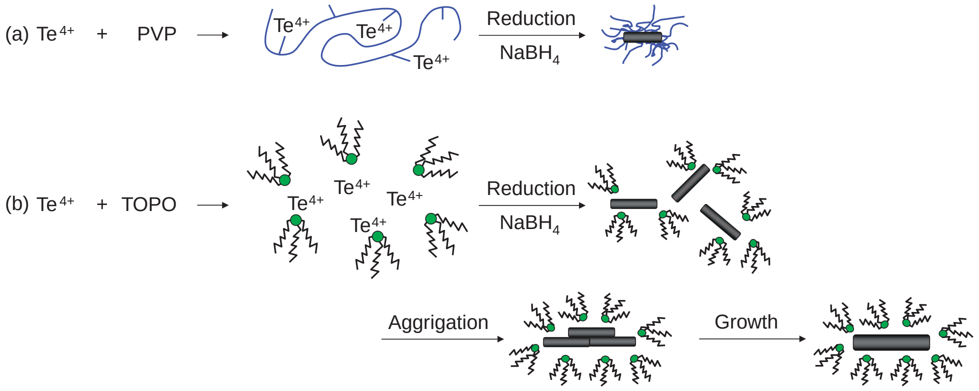


Fig. 1. TEM photographs of Te nanorods prepared by $NaBH_4$ reduction (a) with PVP, (b) with TOPO, and (c) without a protecting agent.



Scheme 1. Proposed mechanism for the formation of Te nanorods in the presence of a protecting agent: (a) PVP and (b) TOPO.

before reaction with $NaBH_4$ because the size and shape of the resulting nanorods are not so uniform without stirring the reaction mixture long enough before addition of the $NaBH_4$ solution. PVP coordinates to Te^{IV} ions by chelate formation (polymer effect)[25,26] better than TOPO. The chelating polymer effect of PVP is maintained not only during but also after the reduction, which could result in smaller size Te nanorods due to effective protection (Scheme 1). A similar effect with PVP on the formation of metal nanoparticles has already been proposed.[27,28]

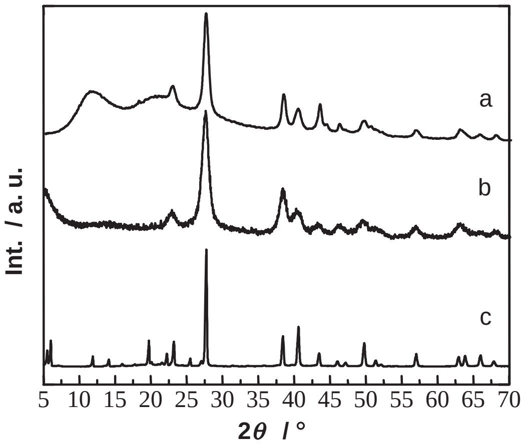


Fig. 2. XRD patterns of the Te nanorods or solid prepared by $NaBH_4$ reduction by using (a) PVP and (b) TOPO, and (c) without a protecting agent.

XRD patterns of Te with PVP and TOPO, and without a protecting agent are shown in Figs. 2a, 2b, and 2c, respectively. The three patterns are principally the same as each other and consistent with that of the hexagonal close-packed structure of bulk Te except for broad peaks attributed to PVP at $2\theta = 12$ and 21° in Fig. 2a. The crystalline sizes, calculated by Scherrer's equation based on the half width of XRD peaks, were 11, 7, and 33 nm for the three samples, respectively. The crystalline sizes calculated by Scherrer's equation were smaller than the average sizes of Te nanorods observed directly by the TEM photographs (10×30 nm, 24×106 nm, and more than 1 μm, respectively). However, this is opposite to relationship between the size calculated by Scherrer's equation and that observed by TEM photographs that is normally observed.[29] When Te nanomaterials were prepared without heat treatment, we could observe small Te nanoparticles which were unstable under the strong electron beam from the TEM, as mentioned before. After heat treatment for 5 min, however, only large nanorods were observed by TEM. From these results, the crystalline size calculated from XRD measurement is small compared to that observed by TEM, probably because Te nanorods are produced by aggregation and/or co-melting of the nanoparticles.

Synthesis of Bismuth Nanoparticles. Bi nanoparticles were easily synthesized by the similar method to the case of Te nanomaterials by using $BiCl_3$ instead of $Te(OC_2H_5)_4$ as the starting material. Again, stable Bi nanoparticles were not

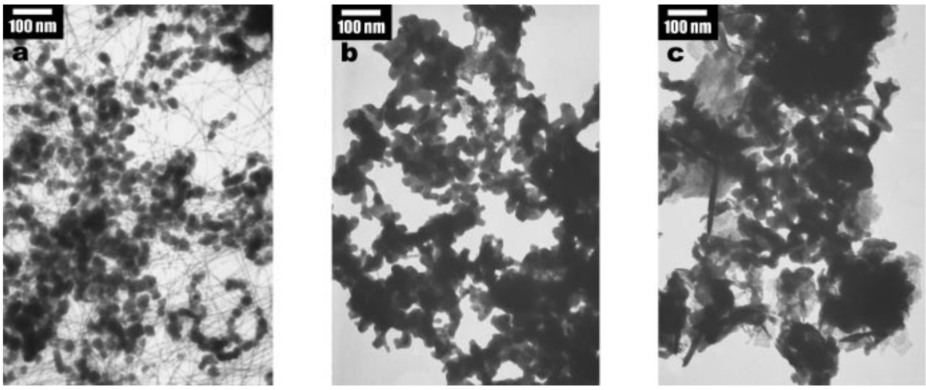


Fig. 3. TEM photographs of Bi nanoparticles prepared by $NaBH_4$ reduction (a) with PVP, (b) with TOPO, and (c) without a protecting agent.

obtained without successive heat treatment. TEM photographs of the Bi nanoparticles[19] obtained by successive heat treatment are shown in Figs. 3a and 3b, indicating formation of well-dispersed nanoparticles with $d_{av} = 29 \pm 8$ and 31 ± 14 nm by using PVP and TOPO as the protecting agent, respectively. By contrast, formation of aggregated nanoparticles with $d_{av} = 46 \pm 22$ nm is observed in Fig. 3c without protecting agents. In the case of Bi nanoparticles, no large difference is observed in size between the particles prepared by using PVP and TOPO as a protecting agent, while aggregates form without protecting agents (Fig. 3c).

It should be noted that PVP-protected Bi nanoparticles (Fig. 3a) contain thin nanowires besides nanoparticles, and that such wires do not exist when TOPO is used (Fig. 3b). EDX spectra taken for both TEM photographs (Figs. 3a and 3b) showed only the presence of Bi. Thus, the nanowires observed in Fig. 3a might be composed of Bi, although it is difficult to selectively prepare only Bi nanowires or to separate nanowires from the mixtures. Yu et al.[18] reported that Bi nanowires with $d_{av} = 6 \pm 3$ nm and a mean length longer than 5 µm were prepared by thermal decomposition of $Bi[N(SiMe_3)_2]_3$ at 476 K in the presence of poly[(1-hexadecene)$_{0.67}$-*co*-(1-vinylpyrrolidinone)$_{0.33}$] and $NaN(SiMe_3)_2$. The Bi nanoparticles with $d_{av} = 11 \pm 2$ nm were produced in this method besides these wires. The d_{av} of the Bi nanowires, which we have obtained in the presence of PVP in the present work, is 6 ± 2 nm and their average length is below 1 µm. Thus, the present technique can easily provide Bi nanowires at a lower reaction temperature than the method reported by Yu et al.[18]

Figures 4a, 4b, and 4c show the XRD patterns of the obtained Bi nanoparticles. The broad peaks at $2\theta = 12$ and 21° are attributed to the PVP protective agent. All other peaks of Bi nanoparticles prepared with or without protecting agents are observed at the same position as those of bulk Bi. Based on the sharpness of the XRD peaks in Figs. 4a, 4b, and 4c, average sizes of Bi nanoparticles were calculated to be 39, 37, and 42 nm, respectively. They are in relatively good agreement with the average sizes observed by TEM.

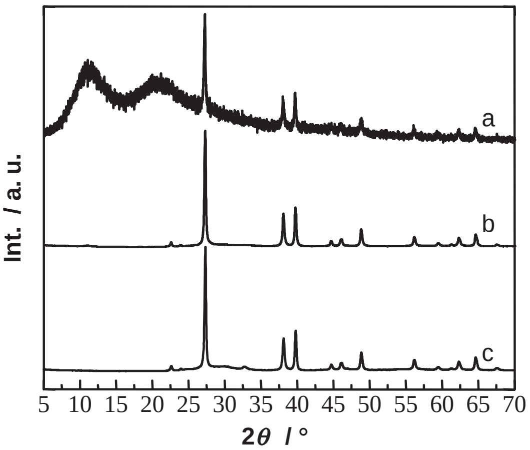


Fig. 4. XRD patterns of the Bi nanoparticles prepared by $NaBH_4$ reduction by using (a) PVP and (b) TOPO, and (c) without a protecting agent.

Synthesis of Bismuth Telluride Nanoparticles. Bi_2Te_3 nanoparticles were synthesized by $NaBH_4$ reduction of $BiCl_3$ and $Te(OC_2H_5)_4$ in ethanol in the presence of PVP or TOPO as protecting agents in a manner similar to that of the Bi nanoparticles and Te nanorods. In the beginning, a protecting agent and metallic precursors were dispersed in solution, and the mixtures were treated by $NaBH_4$ to prepare the Bi_2Te_3 nanoparticles. In the first trial, $BiCl_3$, $Te(OC_2H_5)_4$, and PVP were each separately dissolved of 10 cm^3 ethanol, respectively, and the three solutions were simply mixed in a two-neck flask. To the mixed solutions, a 10 cm^3 $NaBH_4$ solution was added dropwise over 10 min. In this case, the composition and the particle diameter of the obtained Bi_2Te_3 were not uniform. Based on previous results, both Bi^{III} and Te^{IV} ions must strongly interact with protective agents before reduction with $NaBH_4$ in order to prepare small, uniform Bi_2Te_3 nanoparticles.

Finally, we discovered the appropriate mixing procedure of metal ions and the protective agent. The ethanol solutions containing the Bi^{III} and Te^{IV} salts were mixed in a two-neck flask under purified N_2 and stirred for about 1 h. To these mixtures, the ethanol solution of PVP was added, and the resulting mixture was stirred for over 3 h so that PVP could fully coordinate to the metal ions. An ethanol solution of $NaBH_4$ was then added dropwise to the mixture at 273 K over a 10 min period, and the mixture was gradually heated up to the room temperature and then to the boiling point with an oil bath. Reflux was maintained for 1 h. The Bi_2Te_3 nanoparticles prepared by this method are stable as a dispersion for over one year under nitrogen. In other words, PVP must be coordinated to both Bi^{III} and Te^{IV}

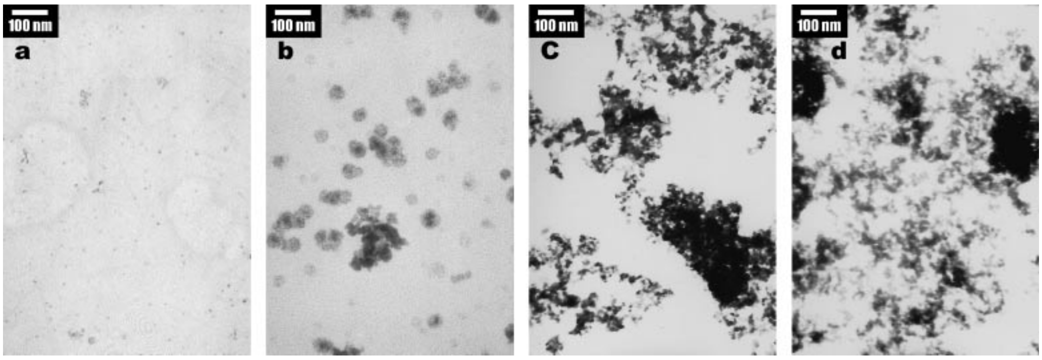


Fig. 5. TEM photographs of Bi_2Te_3 nanoparticles prepared by $NaBH_4$ reduction (a) in the presence of PVP with successive heat treatment at 351 K in ethanol, and (b) at 471 K in ethylene glycol, (c) in the presence of TOPO with successive heat treatment at 351 K in ethanol, and (d) in the absence of a protecting agent with successive heat treatment at 351 K in ethanol.

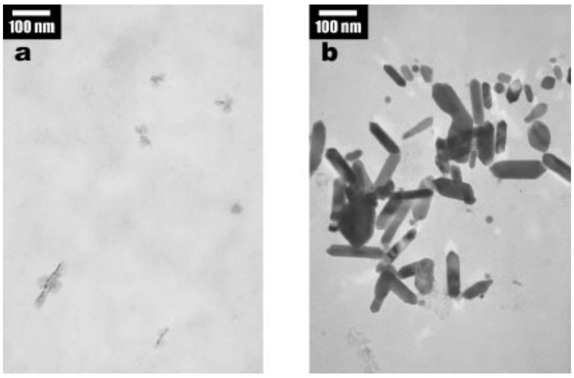


Fig. 6. TEM photographs of Bi_2Te_3 nanoseeds prepared by $NaBH_4$ reduction immediately after addition of PVP (a) without successive heat treatment, and (b) with successive heat treatment at 351 K in ethanol for 1 h.

ions and heating of the material in solution is required.

Growth and Characterization of Bismuth Telluride Nanoparticles. Figure 5a shows the TEM photograph of the obtained Bi_2Te_3 nanoparticles prepared by $NaBH_4$ reduction and successive heat treatment in refluxing ethanol. The average particle size is 7 ± 5 nm. These nanoparticles had a composition of 2.00:3.00 in molar ratio of Bi:Te based on ICP analysis. The same procedures were applied to the preparation of Bi_2Te_3 using TOPO as a protective agent instead of PVP. Based on the TEM photograph of TOPO-protected Bi_2Te_3 nanoparticles, shown in Fig. 5c, d_{av} of the separated particles was calculated to be 23 ± 9 nm, since the particles were strongly aggregated because of poor protecting ability of TOPO. Based on ICP analysis, the composition is 2.00: 2.95 of Bi:Te. Without protecting agent, only aggregates were produced, as shown in Fig. 5d.

In the synthesis of Bi_2Te_3 nanoparticles described above, the mixture of Bi precursors, Te precursors and PVP in ethanol was stirred well for 3 h before addition of $NaBH_4$ solution for reduction. When the $NaBH_4$ solution was added immediately after mixing the metal precursor solutions with the PVP solution, only Bi_2Te_3 nanorods formed as shown in Fig. 6a. It is thought that the strong crystalline properties of small Te nanorods could promote the growth of Bi_2Te_3 nanomaterials along the shape of Te nanorods. The EDX spectrum of these nanorods showed that they were composed of Bi_2Te_3, although the shape might be attributable to Te nanorods or nanowires described previously. Heating the nanorods in refluxing ethanol for 1 h gave Bi_2Te_3 nanorods shown in Fig. 6b. The length of the nanorods is between 50 to 150 nm which is similar to those without heat treatment. However, the width of the nanorods after heat treatment is 30 to 80 nm, which is wider than those without heat treatment (20–30 nm). In other words, the nanorods only grow wider upon heating.

Table 1. Effect of Heat Treatment of Bi_2Te_3 Nanoparticles in a Refluxing Solvent upon the Size

Protecting agent	Heat treatment/K	Average diameter/nm	
		TEM	XRD
PVP	351	7 ± 5	ca. 2
PVP	471	37 ± 7	35
TOPO	351	23 ± 9	24
None	351	aggregated	6

In order to clarify the effect of heat treatment on the growth of nanomaterials, dispersions of PVP-protected Bi_2Te_3 nanoparticles were heated in refluxing ethylene glycol. From TEM, d_{av} of the nanoparticles is 37 ± 7 nm, as shown in Fig. 5b. Thus, heating at higher temperatures causes aggregation.

The effect of heat treatment can be summarized as follows (Table 1). If the $NaBH_4$ reduction was carried out for the mixtures after the contact of precursor metal ions were allowed to react fully with PVP, the nanoparticles obtained without heat treatment at room temperature were 5 to 10 nm in size, which was directly observed by TEM using a low voltage and current density. An attempt to take a TEM photograph by using enough voltage and current density was unsuccessful because the nanomaterials disappear from the grid, i.e., they probably melted under the strong electron beam used to take the photograph. When heated in refluxing ethanol, in contrast, a TEM photograph was acquired, as shown in Fig. 5a (see above). However, the Bi_2Te_3 nanoparticles that were heated in refluxing ethanol were nearly the same size as those prepared without heat treatment, but were apparently more stable against electron beam irradiation. Heating at higher temperatures in ethylene glycol afforded larger particles as mentioned above.

In order to measure the crystalline size of the obtained nanoparticles, XRD patterns were measured. The measured XRD

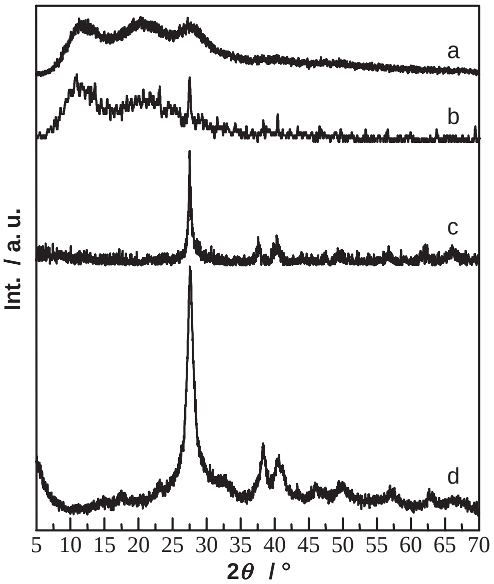


Fig. 7. XRD patterns of the PVP-protected Bi_2Te_3 nanoparticles prepared by $NaBH_4$ reduction (a) with successive heat treatment at 351 K in ethanol and (b) at 471 K in ethylene glycol, and (c) that of TOPO-protected Bi_2Te_3 nanoparticles, and (d) that of Bi_2Te_3 prepared without a protecting agent.

patterns are shown in Fig. 7. The PVP-protected Bi_2Te_3 nanoparticles after heat treatment in refluxing ethanol have very broad peaks (Fig. 7a), beside the peaks at $2\theta =$ ca. 13 and 17° that are attributed to PVP based on the patterns with TOPO (Fig. 7c) and without a protecting agent (Fig. 7d). The broad peaks were attributed to the small size and/or low crystallinity of PVP-protected Bi_2Te_3 nanoparticles. Higher crystallinity of PVP-protected Bi_2Te_3 nanoparticles is desirable for high thermoelectric performance because the thermoelectric properties, in general, are improved by increasing the degree of crystallinity of the materials. Thus, we tried to control the crystallinity by heating the dispersed Bi_2Te_3 nanoparticles in the refluxing solvent. The very broad peak at $2\theta =$ ca. 27° in Fig. 7a shows that the Bi_2Te_3 nanoparticles have a low crystallinity after heat treatment at 351 K in refluxing ethanol. When Scherrer's equation was used to analyze the XRD peaks, the crystalline size of Bi_2Te_3 nanoparticles was calculated to be about 2 nm. This value is much smaller than d_{av} obtained from TEM photograph (7 ± 5 nm). In contrast, from analysis of the XRD peaks for the PVP-protected nanoparticles prepared by heating in refluxing ethylene glycol (Fig. 7b) the size is 35 nm, which is consistent with the value calculated from TEM photograph (37 ± 7 nm). In the case of TOPO-protected nanoparticles, the size observed by TEM photograph (23 ± 9 nm) is near that calculated from the XRD peaks (24 nm), as summarized in Table 1.

Only in the case of PVP-protected Bi_2Te_3 nanoparticles treated by refluxing ethanol was the size that was calculated from XRD peak much smaller than that from the TEM photograph. This difference is due to either the small size of crystalline parts in amorphous Bi_2Te_3 or the aggregation of small crystalline grains. It should be noted again that the Bi_2Te_3 particles prepared without heat treatment were very unstable under strong electron beam and TEM photograph could not be taken. We thought the disappearance of Bi_2Te_3 nanomaterials under strong electron beam was due to melting and evaporation of Bi_2Te_3 because of the rather amorphous structure of the nanomaterials without heat treatment. However, we have succeeded in taking HR-TEM of Pd/Te alloy nanomaterials recently,[30] i.e., even small particles have a crystalline structure and large nanomaterials have polycrystalline structures. From these findings, we could extrapolate that the large nanomaterials of Bi_2Te_3 prepared by heat treatment are polycrystalline materials formed by aggregation and/or co-melting of small nanoparticles. Thus, heat treatment in refluxing ethanol and ethylene glycol improves the crystallinity of the nanoparticles with the growth of crystalline size by aggregation and/or co-melting of small nanomaterials. In other words, the crystallinity as well as the size of Bi_2Te_3 nanoparticles may be controlled by heat treatment in refluxing solvents at various temperatures.

Conclusion

Though there are some reports on the Bi_2Te_3 nanowires and nanorods, the syntheses of Bi_2Te_3 nanoparticles[19] on the order of a single nanometer in size have not been reported to the best of our knowledge, probably because Bi_2Te_3 nanoparticles are easily oxidized by air. Here, we have successfully synthesized Bi_2Te_3 nanoparticles on the order of a single nanometer by reduction with $NaBH_4$ under nitrogen in the presence of PVP and successive heat treatment. For the syntheses of Bi_2Te_3 nanoparticles, the solutions of both Bi and Te precursors were mixed with a PVP solution and the mixture was stirred for long time, ca. 3 h, to ensure that both metal ions are fully coordinated by PVP. The importance of the strong chelating coordination of PVP is supported by the fact that use of PVP affords smaller nanoparticles than TOPO, which is a low molecular weight protecting agent. Heat treatment also improved the stability of Bi_2Te_3 dispersions by suppressing oxidation in solution via growth of the particles and by increasing the crystalline size, which is suggested by comparing the sizes calculated from XRD peaks and those observed in TEM photographs. Using a similar method, Te nanorods and Bi nanoparticles have also been synthesized by slightly altering the heating time. In order to synthesize the protected Bi, Te, and Bi_2Te_3 nanometer-sized materials, it was shown that the protecting agent must strongly coordinate to the metal ions before the reduction reaction, and that the nanomaterials must be heated after the reduction reaction. The dispersions of PVP-protected Bi_2Te_3, Te and Bi nanoparticles can be cast on a glass plate to form self-standing films. In other words, parts of devices containing Bi_2Te_3, Te, or Bi nanomaterials can be fabricated. Investigations of the thermoelectric properties of such films are now in progress.

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