Preparation of Protected Nanoparticles of Bismuth Telluride by Laser Ablation in Solution

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Bismuth telluride (Bi_2Te_3) nanoparticles were prepared by laser ablation in the presence and absence of protective agents. Addition of protective agents could decrease the size of particles, and improve the particle size distribution as well as the colloidal dispersion stability. XRD and HR-TEM have clarified that the Bi_2Te_3 nanoparticles, thus prepared, have a rhombohedral structure.

As energetic and environmental problems become serious recently, the thermoelectric conversion is expected as an useful advanced technology from a viewpoint of effective use of fossil fuel energy. Thus, this technology can be used for recovery of energy from the exhaust heat at relatively low temperature, which is produced by automobiles, power stations, and plants.[1] Bismuth telluride could be the most effective among thermoelectric materials currently available for thermoelectric application below 200 °C. However, the conventional method for preparation of bismuth telluride is based on co-melting of the corresponding metal elements at elevated temperature under special conditions.[2] Recently a few methods were proposed for preparation of bismuth telluride particles aiming the preparation in low cost and low energy. Groshens et al.[3] reported the preparation of Bi_2Te_3 nanoparticles by reaction of $Bi(NMe_2)_3$ and $(Me_3Si)_2Te$ in hexane at -30 °C. Ritter[4] reported the preparation by direct reduction of $Bi_2Te_3O_9{\cdot}xH_2O$ precursors at 275 °C under H_2. Deng et al.[5,6] reported the reduction of $BiCl_3$ and Te powder with KBH_4 in a Teflon autoclave at 100–180 °C for the same purpose. However, these procedures require extra treatments after the reactions and are difficult to control the shape of products. As the thermoelectric properties of Bi_2Te_3 are improved by formation of superlattice structure,[7] the structural arrangement is very effective for improvement of thermoelectric properties of Bi_2Te_3. Therefore, the Bi_2Te_3 nanoparticles, the structure of which can be easily controlled by the synthetic method, are expected to show very interesting thermoelectric properties.

Recently, much attention has been paid to the laser ablation in solution, which provides a new approach to produce nanoparticles.[8,9] Colloidal dispersions of nanoparticles can be prepared without boiling of the solution from any kind of target materials in this method. Moreover, no protective agent is required in general, and thus, the prepared particles have clean surfaces. Here, we report the preparation of Bi_2Te_3 nanoparticles by laser ablation in solution. To our knowledge, this is the first report of the preparation of Bi_2Te_3 nanoparticles by laser ablation.

The 1064-nm output of a CW Q-switched Nd:YAG laser with a pulse energy of 0.8 mJ/pulse was used as an irradiation source. The laser was operated at 3 kHz and the target was ablated by the focused laser light passing through an upper opening of the cell, above which a lens was placed to focus the light at a correct place. The Bi_2Te_3 target, prepared by pressing amorphous Bi_2Te_3 powders and washed with distilled water before laser ablation, was placed in a quartz cell containing 75 cm^3 dimethylformamide (DMF). The protective agents, when used, were dissolved into the solvent before laser irradiation. Ethylenediamine (en), thiophenol (PhSH), polyethyleneimine (PEI), and poly(*N*-vinyl-2-pyrrolidone) (PVP) were used as an protective agent in the present experiments. The solutions were stirred with a magnetic stirrer during irradiation. The size of nanoparticles prepared was measured with transmission electron micrographs (TEM). Crystal structure of the nanoparticles was measured with X-ray diffraction (XRD).

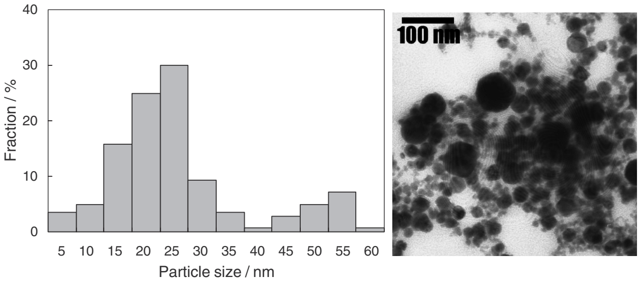

Figure 1. TEM micrograph and size distribution histogram of the bismuth telluride nanoparticles prepared by laser ablation in the absence of a protective agent.

Figure 1 shows TEM micrograph and size distribution histogram of the Bi_2Te_3 nanoparticles prepared by laser ablation in the absence of protective agent. The samples for TEM measurement were prepared by drying-up the colloidal dispersions of Bi_2Te_3 nanoparticles under vacuum for 24 h. The average particle diameter and the standard deviation are 23.4 and 12.6 nm, respectively. The particles are random in size and form aggregates. Because the solution does not contain protective agents, the particles generated by laser irradiation easily grow to form large particles by aggregation.

Figure 2 shows TEM micrographs of the Bi_2Te_3 nanoparticles prepared in the presence of protective agents. In the presence of en and PhSH as protective agents, average particle diameters are 23.1 and 28.8 nm, respectively. In addition, the particles aggregate with each other to form a kind of network, and a little change in a particle diameter was observed depending on the reaction conditions. In the presence of PEI and PVP as protective agents, on the other hand, average particle diameters are 12.7 and 14.6 nm, respectively. Thus, the protective agents of high molecular weight such as PEI and PVP have function to decrease the particle size. In addition, colloidal nanoparticles are well dis-

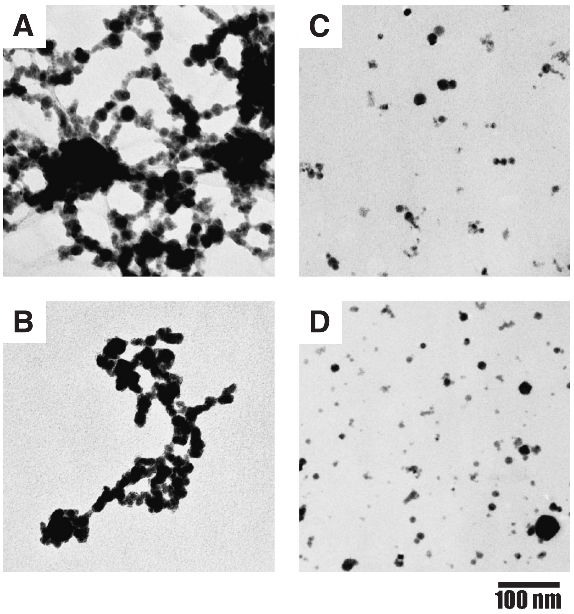

Figure 2. TEM micrographs of the bismuth telluride nanoparticles prepared by laser ablation in the presence of en (A), PhSH (B), PEI (C), and PVP (D) as protective agents at 0.5 w% concentration.

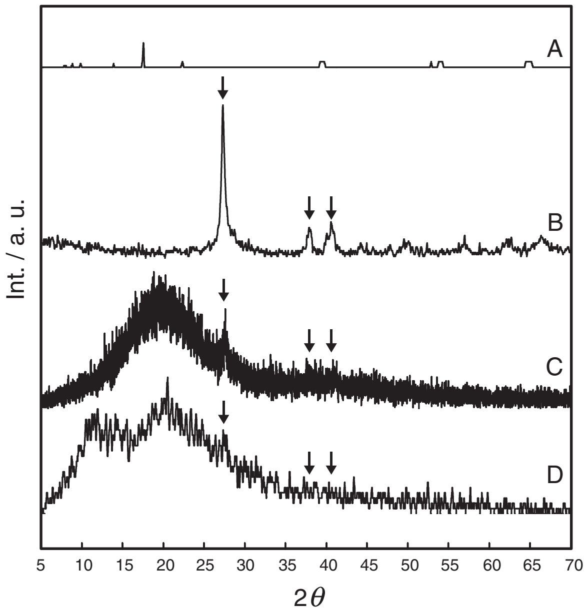

Figure 3. X-ray diffraction patterns of the target of amorphous bismuth telluride (A), and bismuth telluride nanoparticles prepared by laser ablation in the absence of protective agent (B), and in the presence of PEI (C) and PVP (D).

persed, and have a narrow size distribution. In fact, the colloidal dispersions of Bi_2Te_3 nanoparticles form precipitates in several day in the former case, while they keep their original dispersed state over a month in the latter case. The molecular weight of the protective agent is considered as an important factor to control the stable dispersity.

Generally, the protective agents of low molecular weight can stabilize the colloidal particles by single or double coordination on the particle surface, and have a low steric stabilization effect. On the other hand, the protective agents of high molecular weight can stabilize them by multiple coordination, and have a high steric stabilization effect.[10] Thus, in the present case the low molecular weight ligands like en and PhSH cannot sufficiently stabilize the dispersion of Bi_2Te_3 nanoparticles, while the high molecular weight ligands like PEI and PVP can do. In addition, the multiple coordination of high molecular weight ligands like PEI and PVP can be effective in controlling the particle size of Bi_2Te_3 nanoparticles, although such nonconductive polymers may influence the thermoelectric properties.

Figure 3 shows X-ray diffraction patterns of Bi_2Te_3 target and Bi_2Te_3 nanoparticles prepared in solution by laser ablation in the presence and absence of protective agents. The pattern of Bi_2Te_3 target (Figure 3) is completely different from those of Bi_2Te_3 nanoparticles prepared by laser ablation. Although the XRD peaks of Bi_2Te_3 nanoparticles prepared in the presence of protective agents are much weaker and broader than that in the absence of a protective agent, their patterns are the same, and are consistent with those reported by both Ritter[4] and Deng et al.[5,6] except the strong broad peaks attributed to the protective polymers.

As mentioned, the XRD patterns of the bismuth telluride nanoparticles prepared by laser ablation are much stronger than that of the bulk target, and those peak positions are also entirely different from this one. This result suggests that the laser ablation gives crystalline nanoparticles from amorphous raw materials. We regard this rearrangement phenomenon of both bismuth and tellurium atoms in a crystal structure as caused by heat at high temperature during the ablation.

In conclusion, we have succeeded in preparing the Bi_2Te_3 nanoparticles by laser ablation. The stability of colloidal particles increased by addition of the protective agent with high molecular weight, while the aggregation and precipitation of the particles occurred when protective agents with low molecular weight were used instead of that of high molecular weight. The Bi_2Te_3 nanoparticles prepared by laser ablation have a rhombohedral structure based on the results of XRD measurements, The crystallization of nanoparticles by laser ablation will be a great advantage of the present method, which could be applied into various fields.

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