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Scalable synthesis of nanostructured Bi-Te system for an efficient thermoelectric material

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Abstract - Thermoelectric materials (TE) are increasingly becoming preferred alternatives for applications such as power generation and refrigeration Nanostructured TE materials proved to be efficient ones with high figure of merit (ZT). For Bi-Te system, a simple solvothermal route has been employed using different solvents. Methanol has shown promising phase purity as compared to other solvents. The as-synthesized powder is further heat treated to get a pure phase sample.

I. INTRODUCTION

Thermoelectrics enable the direct conversion of heat into electricity and vice versa, offering an alternative opportunity to address the upcoming energy crisis. The prominent advantages of thermoelectric energy conversion includes no moving parts, zero emission, and long working life which enables thermoelectric devices with wide applications. In this regard, efforts have been made to enhancing the conversion efficiency, evaluated by the dimensionless figure-of-merit (ZT), which is proportional to the power factor ($S^2\sigma$) and inversely proportional to the thermal conductivity (κ) [1-3]. Bi_2Te_3 and similar compounds potentially possess large $S^2\sigma$, and low κ thereby act as the dominant thermoelectric candidates for low temperature (200 K - 500 K) power-generation and refrigeration applications [4-5]. One way to manipulate thermoelectric properties is introducing nanostructuring of existing materials, compared to bulk counterparts. Reducing the dimension provides enlarged band gap of nanomaterials because of quantum confinement effect. In addition, phonon scattering for nanomaterials facilitates an ultra-low κ [6-7]. For these reasons, we employed nanostructuring to enhance the thermoelectric performance of Bi_2Te_3 systems. For the synthesis of $Bi\mathbf{2}Te\mathbf{3}$, various methods are reported in the literature e.g. solid state reaction, electrodeposition, mechanical alloying, chemical vapor deposition etc. [8-12]. But each of these methods has some limitations. For example, solid state reaction route is known to give submicron sized grains, which are less effective in scattering phonons on all length scales [8]. Chemical vapor deposition gives nanostructured materials but the quantity is very less and cannot be scaled up for commercial applications [12]. On the contrary, solvothermal route is known to produce nanostructured powders in large amount [13-15]. Hence solvothermal route is employed for the synthesis with different solvents.

II. EXPERIMENTAL

All of precursors, reducing agents, solvents and surfactants were purchased from Alfa Aesar and were used without further purification. $Bi(NO_3)_3$ and Te powder were used as precursors for Bi and Te in the solvothermal synthesis. The stoichiometric ratio of Bi:Te (2:3) was put in a Teflon lined autoclave, which was filled with solvent upto 80% of its volume. Different solvents were employed for the synthesis of Bi_2Te_3 nanostructures such as water, ethylene glycol, ethanol and methanol. Sodium Hydroxide (NaOH) has been used as an alkali modifier; sodium borohydride ($NaBH_4$) and trioctylphosphine (TOP) were the reducing agents along with polyvinylpyrolidone (PVP) which has been used as a surfactant to control the structural growth. After adding sufficient amount of reducing agent and surfactant in the vessel, the autoclave was immediately sealed and heated up to 160°C for 20h, followed by natural cooling to room temperature. The obtained precipitates were washed several times with acetone, distilled water and ethanol, and then dried in vacuum for 10h at 150°C.

The phase determination was done by collecting XRD patterns using CuKα radiation in Rigaku MiniFlexII X-Ray diffractometer. Relevant patterns were recorded over a 2θ range of 10-80°. Raman spectrum was recorded using Ar ion laser in the wave number range of 30-200cm^{-1}. Microstructural characterization of the as-synthesized powder sample with best phase purity was carried out by recording images at different magnifications under Scanning Electron Microscope (SEM). Fourier Transform Infrared Radiation spectroscopy (FTIR) was used to know if any additive is present on the obtained morphology. Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) curves were obtained to know mass and heat changes in samples.

III. RESULTS AND DISCUSSION

XRD patterns of as-prepared powders using different solvents are shown in Fig.1. With ethanol and water as solvents, mixed phases such as Bi_2O_3 and Bi_4Te_3 were observed along with Bi_2Te_3 phase. For the case of ethylene glycol, additional peaks corresponding to Bi_2O_3 phase along with expected Bi_2Te_3 phase. But with methanol, all peaks were indexed to hexagonal phase of Bi_2Te_3. This is attributed to complete reduction of Bi and Te precursors by the reducing agents in methanol as compared to other solvents leading to crystalline Bi_2Te_3 phase. There were no other reactions possible except the combination of Bi^{3+} with the reduced Te^{2-} ions when methanol was used as a solvent. Hence, this poses methanol as the comparatively best solvent for the solvothermal synthesis. However, employing different solvents in the synthesis procedure was to bring out the differences in the final product based on their functionality. Further, Fig.2 shows the recorded Raman spectra of as-synthesized powder. Bulk Bi_2Te_3 has shown rhombohedral crystal structure with five atoms per unit cell and there are 15 lattice vibration modes out of which, three are acoustic and 12 are optical phonons. There are four Raman active modes: $E_g^1, A_{1g}^1, E_g^2, A_{1g}^2$ at wavenumbers 36.5, 62.0, 102.3 and 134.0 cm^{-1} respectively [16]. In Eg, the atoms vibrate in the basal plane, while in A1g, the atoms vibrate along c_H. The A_{1g}^1 and E_g^1 vibrations occur at lower frequencies than A_g^2 and E_g^2. The latter modes, where the outer Bi and $Te^{(1)}$ atoms move in opposite phase, are mainly affected by the forces between Bi and $Te^{(1)}$ atoms[17]. In our present work, Raman peaks were observed at 60.22, 100.73 and 133.43cm^{-1} which are well consistent with the reported literature for Bi_2Te_3[16,18].The lower frequency peak at around 36.5 cm^{-1} was not observed due to instrument constraint. FTIR spectrum, shown in Fig.3, is recorded to know if any additive is present. A strong absorbance peak at 2350cm^{-1} was observed which corresponds to the phosphine group (P-H bond) [19]. The only source of Phosphine group is TOP, the reducing agent used to reduce Te powder during synthesis. To get rid-off this additive as this caused cracks in the sintered pellets and also resulted in reduced electrical properties, sample was heat treated in vacuum at 350°C for 12h. The temperature was decided by analyzing TG/ DSC curves shown in Fig.4a and 4b with and after removal of phosphine (P-H) group respectively. In Fig.4a, there is a huge bump in the DSC plot as an exothermic peak at around 350°C while for heat treated sample, this peak was eliminated as in Fig.4b. This shows that the exothermic peak corresponds to P-H group and has been removed after heating. The endothermic peak at around 585°C in both plots corresponds to the melting point of Bi_2Te_3. Microstructural investigations are done by recording SEM images at low and high magnifications as shown in Fig.5.

IV. CONCLUSION

A simple and scalable solvothermal route has been employed to synthesize Bi_2Te_3 nanostructures using different solvents. Methanol as a solvent has showed better phase purity when it is compared to other solvents, as it was confirmed by XRD, Raman spectroscopy. Microstructural investigations posed nanoparticles of as-synthesized powder to be a prominent candidate which could demonstrate phonon scattering to obtain low thermal conductivity.

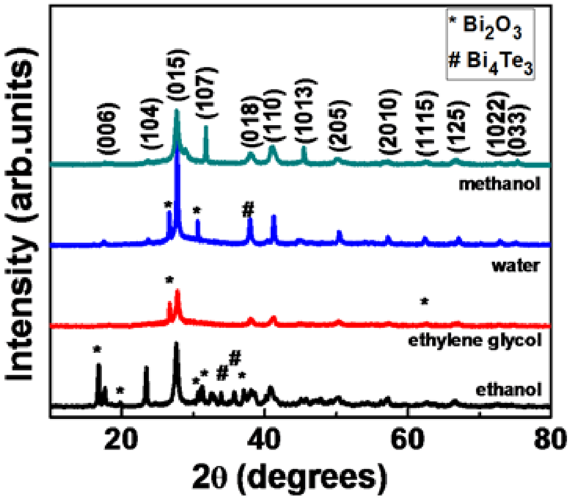

Fig.1: XRD pattern of the as prepared samples using different solvents. All peaks indexed to hexagonal Bi_2Te_3 phase for methanol as a solvent

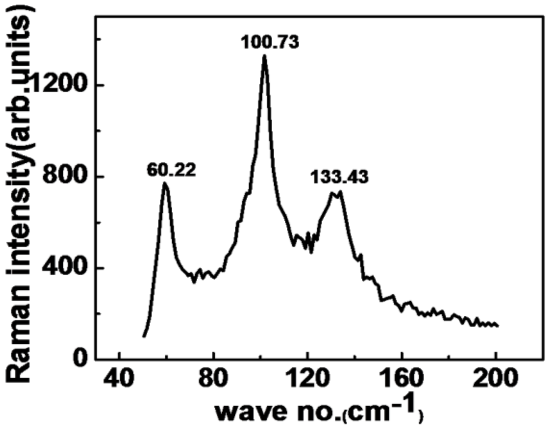

Fig.2: Raman spectra of as synthesized powder with methanol as solvent

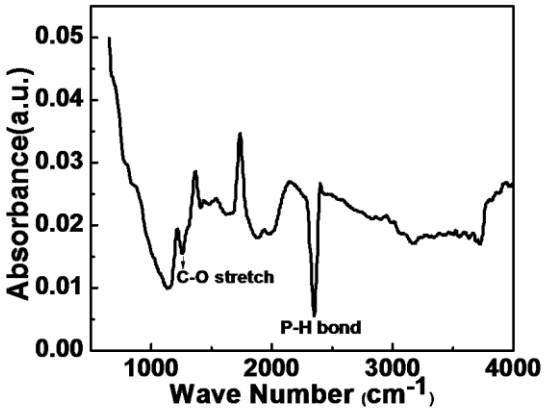

Fig.3: FTIR spectrum of as-synthesized Bi_2Te_3 powder with methanol as solvent

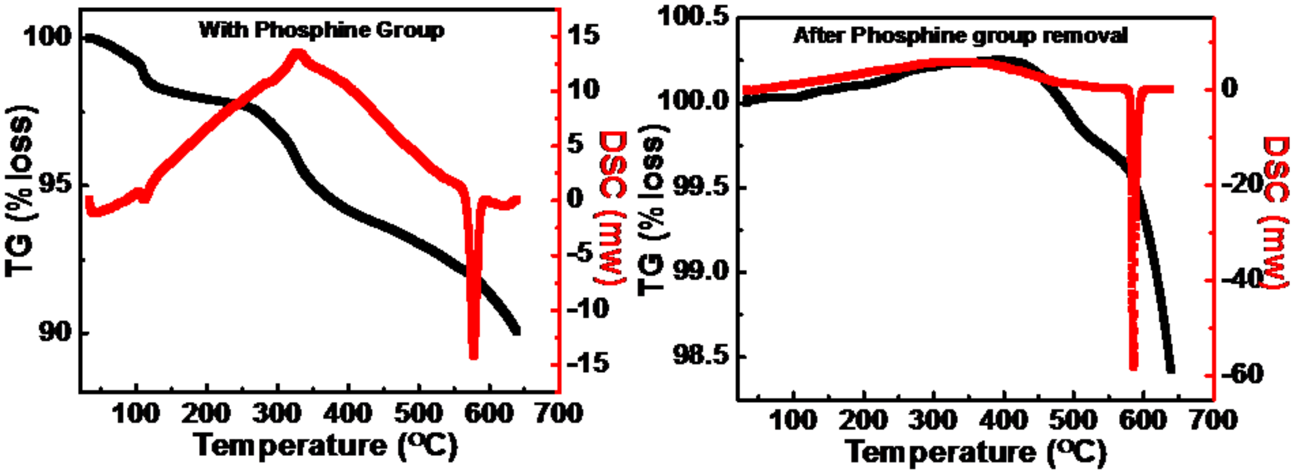

Fig.4: TG/DSC plots for as-synthesized Bi_2Te_3 powder with methanol as solvent with a) phosphine group; b) without phosphine group

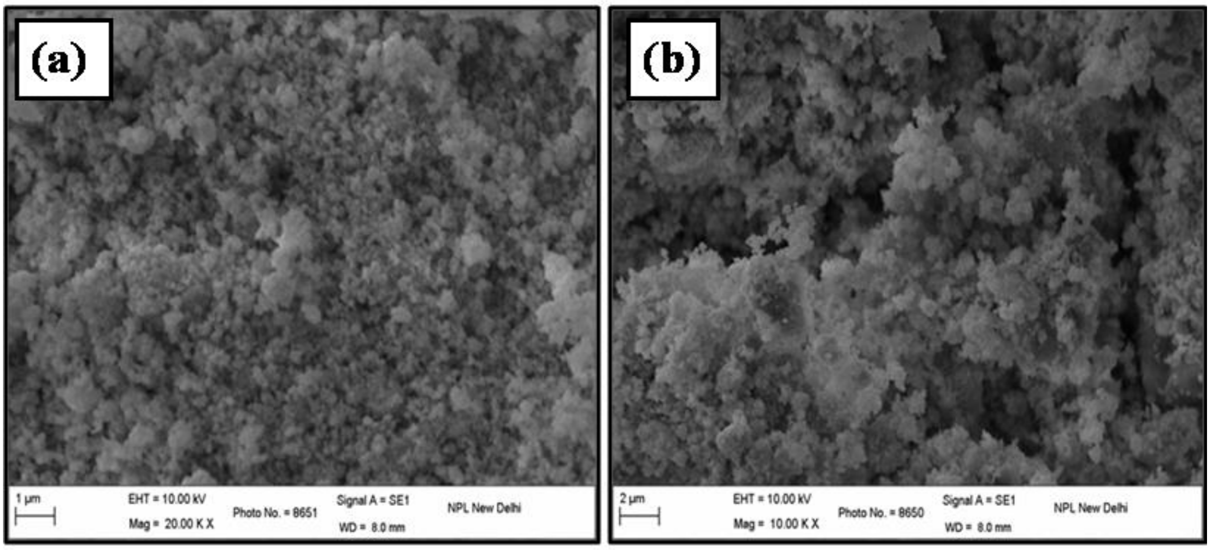

Fig.5: SEM images of as-prepared Bi_2Te_3 powder with methanol as a solvent at (a) low and (b) high magnification

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