Enhancement of Seebeck Coefficient in Bi – PAni Composite Synthesized by In-situ Polymerization

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Abstract
Bismuth–polyaniline composite has been synthesized employing solvothermal and in-situ polymerization technique. The phase structure, composition, and morphology of the synthesized samples were characterized by X-ray powder diffraction (XRD), Fourier transmission infrared spectroscopy (FT-IR) and Ultraviolet visible spectroscopy (UV-vis) respectively. The result shows that the composite consists of Bi particles. Bi particles ranging in size from several tens of nanometers to a few hundred nanometers were dispersed in the SSA-doped PAni matrix. PAni also acted as a protection agent for Bi particles. The Seebeck coefficient of the composite was enhanced due to carrier energy filtering effect.

Keywords
Composite; Electrical Conductivity; Seebeck Coefficient.

I. Introduction
Thermoelectric (TE) phenomena, which involve the conversion between thermal and electrical energy, and provide a method for heating and cooling materials, are expected to play an increasingly important role in meeting the energy challenge of the future. TE materials have great applications in the area of power generation systems, micro-coolers and infra-red detectors [1–2]. Bismuth (Bi) is the most naturally diamagnetic element and has one of the lowest values of thermal conductivity among metals except mercury. The high value of electrical conductivity to thermal conductivity ratio makes Bi as a TE material. Among organic materials polyaniline (PAni) is one of the most promising TE materials. Based on this background we have employed the method of in-situ polymerization for the preparation of the Bi – PAni composite (BPC) for the first time.

II. Experimental
BPC was synthesized by solvothermal and in-situ polymerization using 5-sulfosalicylic acid dehydrate (SSA) (Merck, 99%), aniline GR (Merck, 99.9%), ammonium peroxodisulfate GR (APS) (Merck, 99.5%), ethylene glycol (Merck, 99%), absolute ethanol (Merck, 99%), sodium bismuthate (Sigma Aldrich, 99%) and distilled water (Aqua Prima). In this process 2 gm sodium bismuthate, 100 ml ethylene glycol and 100 ml absolute ethanol were put into a beaker at room temperature. The solution was mechanically stirred for 45 min. Then the resultant solution was transferred into container of 200 ml, which was then put into an autoclave for 24 h at 200^{0}C and cooled down to room temperature. The resultant product was rinsed with absolute ethanol for several times to remove all impurities and to get Bi particles. To prepare BPC doped with SSA, aniline and 40 wt% of Bi particles were dissolved in an aqueous solution containing SSA. An aqueous solution of APS was mixed drop wise to start the oxidation, and the reaction mixture was stirred for 6 hrs below 6 ^{0}C. A dark green precipitate was recovered from the reaction vessel by centrifuge and followed by filtration. Finally, we get the BPC.

X-ray powder diffraction (XRD) measurement was performed using a diffractometer (BRUKER D8 Advance) with Cu-Kα radiation (λ= 1.54182 Å) at room temperature. FT-IR spectra were recorded (Thermo Nicolet Nexus 870) in the range between 400 to 4000 cm^{-1}. The UV–vis spectra of the prepared samples were recorded by a spectrophotometer (UV-180 SHIMADZU) in quartz tube in the wavelength range of 270 – 1100 nm. The prepared samples were pelletized into a rectangular disc (of thickness 2 mm, length 8 mm and breadth 5 mm). The prepared pellet of samples was placed in a holder and connected with wires for thermoelectric measurement. The electrical conductivity of prepared samples was measured by Four-Probe Method (SES instrument model no. DFP-02). Room-temperature thermal conductivity measurements were carried out for the prepared samples using a Hot Disk thermal constants analyser (TPS 2500 S, Sweden). For the measurement of Seebeck coefficient, an auxiliary heater was placed at one end of the sample holder to establish a temperature difference, while the corresponding potential drop was measured by a HP data acquisition system (Model No. 34970A).

III. Results and Discussion
The XRD patterns of Bi particles, PAni and BPC are shown in fig. 1. The formation of Bi is confirmed by the major peaks labelled in the XRD pattern that corresponds to the rhombohedral phase of Bi according to the reported values of JCPDS (No. 05– 0519) data sheet. The XRD pattern reveals that the samples synthesized under above stated conditions are pure bismuth with no impurity. Four broad peaks at 15°, 20°, 25°and 43° for pure PAni are observed. This XRD pattern indicates that PAni is a semi-crystalline solid [3]. Generally polymers are considered to be amorphous, but here the synthesized polymer is showing crystalline structure due to their fibre nature and planar nature of benzenoid and quinoid functional groups. BPC shows same peaks position as in Bi except higher FWHM and changes in 2θ value.

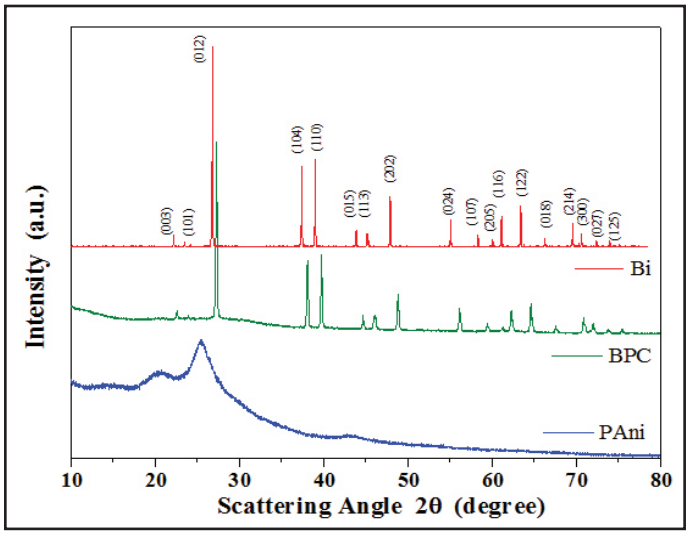

Fig. 1: XRD Patterns of Bi Particles, PAni and BPC.

FT-IR spectra of PAni, Bi and BPC are shown in fig. 2. The explanation of various observed peaks of PAni and BPC is summerized in Table 1. The transition of charge carriers is analysed in benzenoid structure and quinonoid ring of the prepared conducting PAni using UV – visible spectrum. The characteristics absorption of conducting PAni plays a vital role in the utilization of the materials in the optoelectronic applications. The band with peak at 314 nm for the PAni samples corresponds to π-π* transitions of benzenoid ring. The broad bands with peak at 629 nm is due to π-π* transitions of quinine-imine groups [4]. The peak at 464 nm is due to polaron-π* transition and the peak at 922 nm is due to π-polaron transition as shown in fig. 3.

In UV-vis spectrum of BPC, two major peaks at 310 nm and 622 nm are due to π –π* transition and owing to the shifting of electron from benzenoid ring to quinonoid ring respectively. The variations of electrical conductivity (σ) as a function of temperature of the prepared samples are shown in fig. 4. The value of σ for Bi is observed to decrease with the increase of temperature. But for PAni and BPC, the values of σ increases with temperature. So the behaviour of Bi is metallic type, but PAni and BPC shows semiconducting nature.

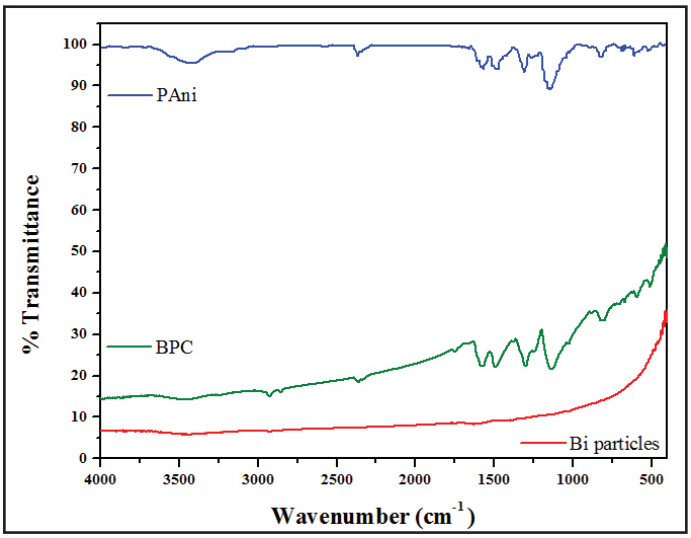

Fig. 2: FTIR spectra of Bi, PAni and BPC.

Table 1: Comparison of FT-IR spectra between PAni and BPC

PAni	BPC	Remarks
Below 1000 cm^{-1}	Below 1000 cm^{-1}	Characteristics of mono substituted benzene (out of plane bending)
1139 cm^{-1}	1128 cm^{-1}	C-H bending vibrations
1300 – 1200 cm^{-1}	1300 – 1200 cm^{-1}	C-N stretching vibrations of primary aromatic amines
1477 cm^{-1}	1486 cm^{-1}	C=N stretching in aromatic compounds
1552 cm^{-1}	1576 cm^{-1}	C-H stretching in aromatic compounds
1700 – 1600 cm^{-1}	1700 – 1600 cm^{-1}	C=C (benzoid) stretching in aromatic nuclei.
2355 cm^{-1}	2358 cm^{-1}	Symmetric C-H stretching vibrations
2912 cm^{-1}	Around 2900 cm^{-1}	Asymmetric C-H stretching vibrations
3416 & 3218 cm^{-1}	3460 & 3230 cm^{-1}	N-H stretching vibrations

At room temperature the thermal conductivity of Bi, PAni, BPC are found to be 7.97 W/mK, 0.143 W/mK and 0.278 W/mK respectively. The temperature variation of Seebeck coefficients (S) is shown in fig. 5. The value of S of BPC, PAni and Bi is found to be 33.34, 5.35 and -73.17μV/K respectively at 305K. It indicates that the majority carriers in PAni and BPC are holes, but in Bi the majority carriers are electrons. The value of S for the composite is found to be higher value than Bi and PANI above 325 K.

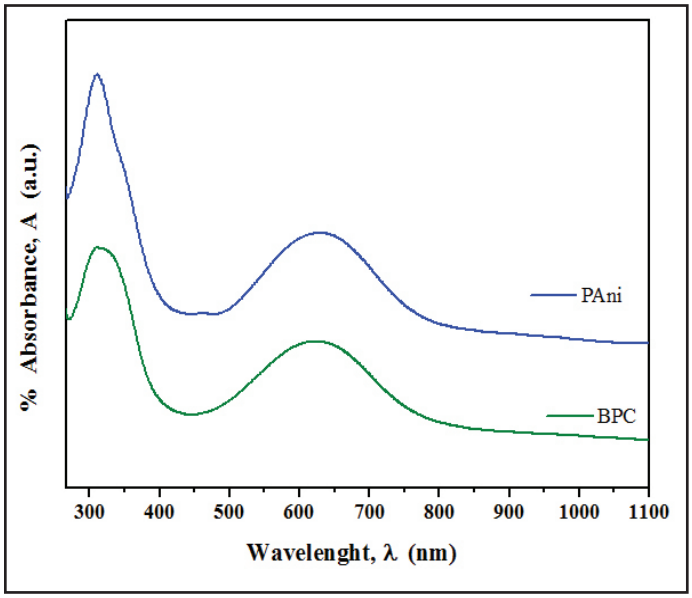

Fig. 3: UV-vis Spectra of PAni and BPC.

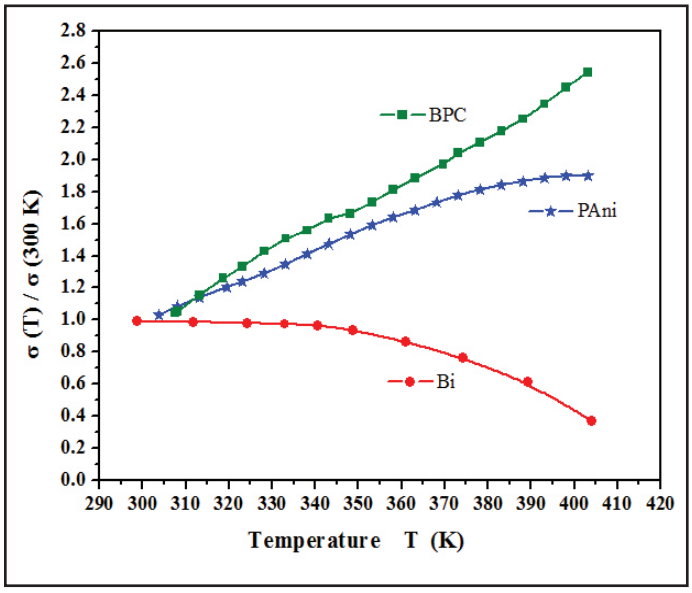

Fig. 4: The Variations of Electrical Conductivity With Temperature.

The enhancement of S is attributed to carrier energy filtering effect. On account of embayed Bi particles, the interface barrier potential is formed between Bi particle and PAni matrices. Low energy carriers are strongly scattered than the high energy carriers (Low energy carrier less than the barrier height are scattered more than the high energy carriers). Since the S depends on the excess energy ($E-E_f$) of the carriers in the composite [5], its value increases with temperature.

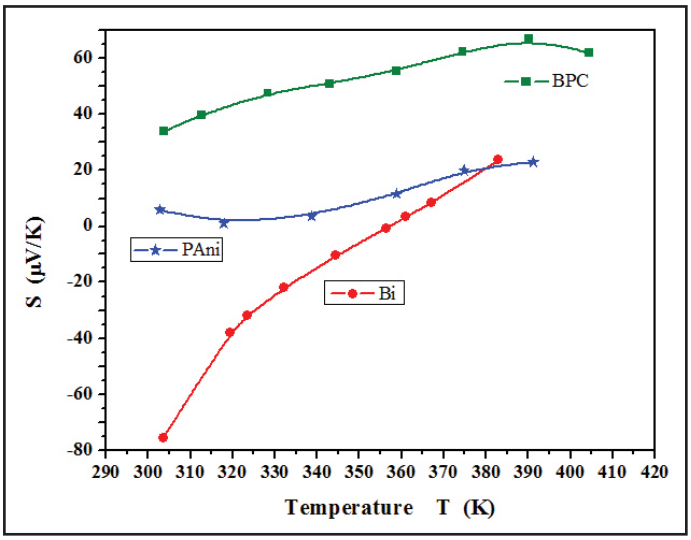

Fig. 5: The Variation of Seebeck Coefficient With Temperature.

IV. Conclusion

To the best of my knowledge BPC has been synthesized by in-situ polymerization for the first time. The Seebeck coefficient is enhanced in BPC as compared to that of PAni, as a result of structural ordering leading to an increase in carrier mobility. At room temperature, the thermal conductivity of the BPC is lower than that of Bi, due to the selective phonon scattering by the interfaces designed in the BPC structure. This structure also supports observations of the electrical transport properties in the system. Hence this study may be quite useful in the design and synthesis of polymer composites for TE applications.

V. Acknowledgement

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