Bi$_2$Se$_3$-PVDF composite: A flexible thermoelectric system

Ashutosh Kumar$^{a,b,*}$, Ravi Kumar$^c$, Dillip K. Satapathy$^a$

$^a$ Soft Materials Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, 600036, India
$^b$ Lukasiewicz Research Network-The Institute of Advanced Manufacturing Technology Wroclawska 37, Poland
$^c$ Department of Metallurgical Engineering Indian Institute of Technology Madras, Chennai, 600036, India

**ABSTRACT**

We report the thermoelectric properties of flexible Bi$_2$Se$_3$-Polyvinylidene fluoride (PVDF) based polymer nanocomposites (PNC) over a temperature range from 250 K to 350 K. The two-dimensional Bi$_2$Se$_3$with nanoplate like structure is synthesized using the reflux method and is dispersed with the PVDF matrix. A significant reduction in the thermal conductivity of the PNC in comparison to the individual phases of Bi$_2$Se$_3$ and PVDF is observed. The overall thermal conductivity value of the PNC is measured to be 0.06 W/m-K at 300 K. An order of magnitude reduction in the thermal conductivity in the PNC is explained using the acoustic impedance model. The Seebeck coefficient and the electrical conductivity are decreasing with the addition of PVDF to Bi$_2$Se$_3$. The figure of merit of PNC is determined to be about 0.004 at 300 K, and the flexible nature of Bi$_2$Se$_3$-PVDF nanocomposites is also demonstrated. The mechanical properties of the PNC are quantitatively measured using nanoindentation technique.

1. Introduction

Flexible thermoelectric (TE) materials are attracting immense research interest due to its potential application in wearable and portable electronic devices. In recent times, several studies have demonstrated the importance of flexible TE materials because it offers the possibility of waste heat recovery from uneven surfaces that has the potential for large area coverage applications. [1-5]. The usefulness of the TE materials is quantified using a dimensionless quantity known as the figure of merit (ZT = $S^2T/\rho\kappa$; where $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ is the thermal conductivity, and $T$ is the absolute temperature). A flexible TE system requires a high value of $S$ and low value of $\rho$ and $\kappa$ for high ZT along with flexibility, which is suitable for portable and wearable electronic devices [6]. The best inorganic material based TE systems like Bi$_2$Se$_3$ and related alloys are rigid; however, polymers are a class a material that offers flexibility along with very low thermal conductivity [7,8]. The TE properties of the polymer alone are not very promising, in general, due to its poor electrical conductivity and Seebeck coefficient values. Several chemical de-doping processes have been adopted to improve the electrical conductivity and Seebeck coefficient in polymers itself; however, it requires several complicated synthesis processes [9-11]. In general, the composite approach has been adopted in the inorganic system to improve the TE properties [12,13]. A similar strategy is adopted to develop flexible TE systems, where composites made of polymers and inorganic systems are investigated and found to show good TE properties [14-18]. Polyvinylidene fluoride (PVDF) is a polymer that offers flexibility along with low thermal conductivity, which is suited for TE materials. Dun et al. demonstrated the n-type flexible TE in Bi$_2$Se$_3$-PVDF composite [2], which shows a power-factor of $\sim 30 \mu$W/(m-K$^2$) at room temperature. However, thermal conductivity in composites is an important parameter that indicates the utility of TE systems. Also, the thermal conductivity in inorganic-organic composites is very interesting because of the mismatch in their elastic properties between inorganic and organic systems [19]. It is worth mentioning that most of the heat in a semi-conducting system is carried by phonons, and phonons can be scattered significantly if materials have different elastic properties [20]. However, research in this direction is not significantly noticed, and a systematic study on thermoelectric properties in the inorganic-organic hybrid system focusing on the thermal conductivity in such composites is required. Here, we present the structural, mechanical, and thermoelectric properties of Bi$_2$Se$_3$-PVDF nanocomposites as a function of temperature in a range from 250 K to 350 K. In particular, a significant reduction in the thermal conductivity of the Bi$_2$Se$_3$-PVDF nanocomposite is a novel outcome of this study and is explained using the acoustic impedance mismatch (AIM) model.
2. Experimental section

Bi$_2$Se$_3$ nanocomposites were synthesized using the reflux method. In a typical synthesis process, 5 mmol of Bi(NO$_3$)$_3$·5H$_2$O (Sigma Aldrich, 99.9%) and 7.5 mmol of Na$_2$SeO$_3$ (Sigma Aldrich, 99.9%) were added to 175 mmol of ethylene glycol. The mixture was stirred vigorously for 30 min and was further refluxed at 240 °C for 5 h. The impurity from the solution was then removed using repeated centrifugation with 2-propanol and ethanol. The precipitate thus obtained was dried overnight in a vacuum oven maintained at 60 °C and a pressure of 100 mbar. Further, to make the nanocomposite, 300 mg of Bi$_2$Se$_3$ and 150 mg of PVDF were mixed with 5 ml DMF (Sigma Aldrich, 99%), and the solution is stirred to make the nanocomposite, 300 mg of Bi$_2$Se$_3$ was drop-cast on a glass substrate and dried for 24 h on a magnetic stirrer. The nanocomposite mixture was then drop-cast on a glass substrate and dried at 80 °C for 6 h in a vacuum oven maintained at 100 mbar. The structural characterization of the pure Bi$_2$Se$_3$, PVDF, and Bi$_2$Se$_3$–PVDF nanocomposite was done using the X-ray diffraction technique using Cu-K$_\alpha$ (λ = 1.5406 Å). Further, the XRD pattern of Bi$_2$Se$_3$ was analyzed using Rietveld refinement through Fullprof™ software. Field emission scanning electron microscope (FESEM) images depict the surface morphology of the Bi$_2$Se$_3$ and Bi$_2$Se$_3$–PVDF nanocomposite samples. The energy-dispersive X-ray spectroscopy (EDX) for the Bi$_2$Se$_3$–PVDF nanocomposite. Further, high-resolution transmission electron microscope is used to investigate the existence of individual phases in the PNC. Thermal transport measurements were done using the physical properties measurement system (PPMS, Quantum Design) from 250 K to 350 K. In particular, the Seebeck coefficient and thermal conductivity were measured using the thermal transport option of PPMS, using a sample of cylindrical shape with 6 mm in diameter and 1.5 mm in thickness. The electrical resistivity of both the sample was measured using the standard four-probe method in PPMS. The bending test is performed on a thin membrane of PNC prepared by the drop-cast method. The mechanical properties of the polymer nanocomposite were studied using the nanoindentation technique (Hysitron).

3. Results and discussion

The X-ray diffraction pattern for Bi$_2$Se$_3$, PVDF, and Bi$_2$Se$_3$–PVDF nanocomposite samples are shown in Fig. 1(a). The diffraction pattern confirms the formation of a pure phase of Bi$_2$Se$_3$. The diffraction pattern confirms the trigonal phase as per the ICDD File no. 9011965. The Bragg’s position and corresponding Miller indices for the peaks are marked. The diffraction pattern recorded for PVDF is also shown in Fig. 1(a). The characteristic 2θ diffraction peak observed at 20.2° corresponds to the sum of the diffraction from planes (110) and (200) of the β-phase of PVDF. This β-phase formation of PVDF is a result of heating the sample at 80 °C. In the nanocomposite sample, the diffraction peaks due to both the Bi$_2$Se$_3$ and PVDF are observed. This confirms that both the phases are preserved in the polymer nanocomposite. The powder XRD pattern of Bi$_2$Se$_3$ is further analyzed using Rietveld refinement [21] procedure by employing Fullprof™ software to estimate the structural information such as the lattice parameters of Bi$_2$Se$_3$. The Rietveld refinement is performed using the R-3m space group, and the refinement pattern for Bi$_2$Se$_3$ is shown in Fig. 1(b). The lattice parameters obtained from the refinement are a = 4.1374 Å, and c = 28.6164 Å, and corresponding refinement parameters are $R_p=8.24, R_w=9.89, R_{wp}=7.62$ and $\chi^2=1.68$. The refinement parameters are well within the acceptable limit.

The surface morphology of Bi$_2$Se$_3$ and Bi$_2$Se$_3$–PVDF nanocomposite are recorded using a field emission scanning electron microscope (FESEM) technique and shown in Fig. 2(a) and (b). The two-dimensional hexagonal nanoplate type structure is observed in the Bi$_2$Se$_3$ system, as shown in Fig. 2(b). The size of each side of the hexagons is close to 1 μm, and few nanocomposites have sizes larger than 1 μm. In the Bi$_2$Se$_3$–PVDF sample, the hexagons are nanocomposites are observed along with the submicron-sized grains corresponding to the β-phase of PVDF. The two-dimensional hexagonal nanoplate type structure is also preserved in the Bi$_2$Se$_3$–PVDF nanocomposite. The energy-dispersive X-ray spectroscopy (EDX) for the Bi$_2$Se$_3$–PVDF nanocomposite is shown in Fig. 2(c). It is noted that along with Bi and Se peaks, the peaks corresponding to C and F are also observed, and the atomic weight percentage is shown in Fig. 2(c). The elemental composition for the pure Bi$_2$Se$_3$ is also shown in the inset of Fig. 2(c), which agrees well with the experimental composition of Bi$_2$Se$_3$.

Further, the high-resolution transmission electron microscope is used to investigate the existence of both the phases in the PNC. The HRTEM images for Bi$_2$Se$_3$ and Bi$_2$Se$_3$–PVDF nanocomposite samples are shown in Fig. 3(a) and (b), respectively. It is noted that we observed the lattice spacing corresponding to Bi$_2$Se$_3$ [0.301 nm (015)] and PVDF [0.426 nm (015)] in the PNC. It further confirms the existence of individual phases of Bi$_2$Se$_3$ and PVDF in the PNC.

The Seebeck coefficient (S), electrical resistivity (ρ), thermal conductivity (κ) and the figure of merit (ZT) as a function of temperature for Bi$_2$Se$_3$ and Bi$_2$Se$_3$–PVDF nanocomposite samples are shown in Fig. 4 (a–d). The Seebeck coefficient of Bi$_2$Se$_3$ is found to increase with an increase in temperature showing the semiconducting nature of the sample. The negative sign of the Seebeck coefficient indicates that the n-type charge carriers have a significant contribution to the electrical conduction and is consistent with the previous report [2]. The decrease in the Seebeck coefficient of the polymer nanocomposite is attributed to the fact that the Seebeck coefficient arises from the weighted contribution from each component in a nanocomposite since PVDF contributes less compared to Bi$_2$Se$_3$ and hence the overall Seebeck coefficient decreases. The value of the Seebeck coefficient at 300 K for Bi$_2$Se$_3$ is $-120$ μV/K, and it decreases to $-98$ μV/K for the nanocomposite.

The electrical resistivity of Bi$_2$Se$_3$ values lies between 0.001 and
0.002 Ohm-m in the temperature ranging from 250 to 350 K. The electrical resistivity of the nanocomposite also follows a similar temperature dependence; however, the resistivity values are higher than Bi$_2$Se$_3$. The increase in the electrical resistivity value of the nanocomposite is due to the presence of sub-micron size insulating PVDF, which decreases the overall carrier concentration as well as restricts the mobility of Bi$_2$Se$_3$ in the system [23].

Polymer materials consist of very low intrinsic thermal conductivity as they consist of a discrete set of individual chains. We have measured the thermal conductivity (κ) of Bi$_2$Se$_3$ and Bi$_2$Se$_3$-PVDF nanocomposite using the physical properties measurement system (PPMS). The thermal conductivity is found to decrease with the increase in temperature for Bi$_2$Se$_3$ and Bi$_2$Se$_3$-PVDF nanocomposite. The κ at room temperature for Bi$_2$Se$_3$ synthesized using the reflux method is 0.23 ± 0.006 W/m-K, which is lower than that of the Bi$_2$Se$_3$ samples synthesized using conventional melting of individual elements [24]. This decrease in κ is attributed to the nanoplate like structure in the system, which enhances the phonon scattering near the boundary of the nanoplates [25]. Further, the κ decreases almost by one order of magnitude to 0.06 ± 0.002 W/m-K for the Bi$_2$Se$_3$-PVDF nanocomposite. It is noted that the thermal conductivity of PVDF is 0.2 W/m-K at room temperature [26], and that of Bi$_2$Se$_3$ is 0.23 ± 0.006 W/m-K. However, the nanocomposite made of these two individual phases reduces the κ significantly. This reduction in the κ may be further ascribed to the mismatch in the elastic properties of the two phases present in the nanocomposite. This significant reduction in the thermal conductivity of the nanocomposite compared to the individual phases present in the system is a crucial observation of this work. It can be understood using the acoustic...
impedance model [27]. The dominating contribution of thermal conductivity is carried by phonons in a semiconducting system. The probability of phonon transmission and reflection coefficient can be estimated if the acoustic impedance ($Z$) for both the phases are known, using the relation [28].

$$Z_i = d_i v_i$$

where $d_i$ is the density, and $v_i$ is the sound velocity for the $i^{th}$ materials. The density and velocity of sound for Bi$_2$Se$_3$ are 6.82 g/cm$^3$, 1996 m/sec, and that for PVDF are 1.78 g/cm$^3$ and 2200 m/s respectively [29, 30]. The acoustic impedance for Bi$_2$Se$_3$ and PVDF is hence 13,612 and 3916, respectively. The probability of phonon reflection ($R_{12}$) and phonon transmission ($T_{12}$) is defined as [28].

$$R_{12} = \left( \frac{Z_2 - Z_1}{Z_1 + Z_2} \right)^2$$

$$T_{12} = \frac{4Z_1 Z_2}{(Z_1 + Z_2)^2}$$

where $R_{12}$ is the probability of phonon reflection at the phase boundary, and $T_{12}$ is the probability of phonon transmission through the phase boundary. The $R_{12}$ and $T_{12}$ calculated using the acoustic impedances ($Z_1$ and $Z_2$) for the Bi$_2$Se$_3$-PVDF nanocomposite is found to be 55% and 45%, respectively. This suggests that due to the difference in acoustic impedance between these two phases in the nanocomposite, around 55% of the phonons gets reflected at the interface between Bi$_2$Se$_3$-PVDF. Along with the addition of the polymorphic phase that reduces the thermal conductivity, the phonons get reflected at the interface between Bi$_2$Se$_3$ and PVDF. Hence a significant reduction in the thermal conductivity is observed, which is less than both the individual phases in the nanocomposite.

The figure of merit estimated using $S$, $\rho$, and $\kappa$ as a function of temperature for the Bi$_2$Se$_3$ and Bi$_2$Se$_3$-PVDF nanocomposite is shown in Fig. 4(d). The ZT value for both Bi$_2$Se$_3$ and Bi$_2$Se$_3$-PVDF is found to increase with the increase in temperature. This is due to the increase in $S$ and a decrease in $\kappa$ with an increase in temperature. The maximum ZT value of the Bi$_2$Se$_3$ sample is 0.026 at 350 K. This lower value of ZT for Bi$_2$Se$_3$ at 350K may be attributed to the high electrical resistivity of the sample owing to the nanoplate size structure. The ZT value of the Bi$_2$Se$_3$-PVDF nanocomposite is approximately 0.004 at 350 K. The ZT value of nanocomposite is found to decrease due to a reduction in $S$ and an increase in $\rho$. However, the addition of PVDF has improved the flexibilivity of the nanocomposite.

To explore the mechanical properties of the polymer nanocomposite, the nanoindentation measurement technique is employed on the PNC pellets. Nearly 9–12 indentation measurements are performed with the varying loads from 1 mN to 4 mN with a load rate of 100 µN/s and a hold time of 10 s on Bi$_2$Se$_3$-PVDF nanocomposite sample. The load-displacement plots for different loads are shown in Fig. 5(a-d). The average value of the load-displacement curve for each load is marked in bold for each load in Fig. 5(a). It is noted that with increasing load, the displacement of the nanocomposite sample increases for 1000 N, 2000 N, and 4000 N; however, the average value of displacement is lower when 3000 N is applied. The indentation measurement is done at different locations of the PNC for every load. The reduction in average displacement for 3000 N may be due to the presence of more Bi$_2$Se$_3$ phases than PVDF. Further, the mechanical parameters like hardness ($H$) and reduced Young’s modulus ($E_r$) are estimated from the unloading line from the load-displacement curves using Oliver-Pharr equations [31]. The average value of $H$ and $E_r$ obtained from nearly 9 to 12 indents corresponding to each load and measured at different locations over the sample surface is shown in Fig. 6(a-d). The parameters quantifying the mechanical properties like $H$ and $E_r$ are found to decrease with increasing the load. This suggests that the polymer nanocomposite sample is less resistant to plastic deformation. Further, the thin free-standing membranes synthesized using the drop cast method is shown in Fig. 6(c). It is noted that the dimensions of the flexible PNC samples used for measuring the thermoelectric properties and showing the flexible nature (Fig. 6(c and d)) are different. It is because of the specific sample size requirement for both the characterization techniques. The flexible nature of the polymer nanocomposite films can be inferred from Fig. 6(d), where the films are manually squeezed without any degradation of the membranes. This concludes that although the ZT value of the
nanocomposite is reduced due to PVDF addition, however, it imparts the flexibility to TE material, which is of interest to the present-day technology.

4. Conclusion

The $\text{Bi}_2\text{Se}_3$ nanoplates are synthesized using the reflux method. The Rietveld refinement of the X-ray diffraction pattern confirms the pure phase formation. The surface morphology confirms the presence of micron-sized hexagonal 2-dimensional nanoplates of $\text{Bi}_2\text{Se}_3$ and sub-micron sized domains of $\beta$-PVDF. The EDX measurement shows that the chemical composition of Bi and Se agrees well with the nominal composition in $\text{Bi}_2\text{Se}_3$. The presence of both the phases in the polymer nanocomposite (PNC) is further confirmed from a high-resolution transmission electron microscope. Seebeck coefficients of the nanocomposites are found to decrease with the addition of PVDF in the nanocomposite and are attributed to the weighted contribution of individual components in the nanocomposite. The thermal conductivity of the PNC decreases by almost an order of magnitude to $0.06 \pm 0.002 \ W/\ m-K$ compared to $\text{Bi}_2\text{Se}_3$, attributed to the difference in the acoustic impedance between the two phases in the nanocomposite. The electrical resistivity of the nanocomposite increases with the addition of insulating PVDF in the system. A figure of merit of 0.004 is obtained at 350 K for the $\text{Bi}_2\text{Se}_3$-PVDF nanocomposite. The mechanical properties of the PNC reveal less resistive nature of the nanocomposite towards plastic deformation with increasing load. The flexible nature of the thermoelectric brings an extra dimension, which is an added advantage for the futuristic flexible thermoelectrics.

Authors declare there is no conflict of interest

A. Kumar and D. K Satapathy designed the experiments. A. Kumar performed the experiments and written the manuscript. A. Kumar, Ravi Kumar and D.K. Satapathy revised the manuscript.

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