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Temperature-Dependent Raman Scattering of Large Size Hexagonal Bi₂Se₃ Single-Crystal Nanoplates

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Abstract: Bi₂Se₃ has extensive application as thermoelectric materials. Here, large-scale Bi₂Se₃ single-crystal hexagonal nanoplates with size 7.50–10.0 μm were synthesized successfully by hydrothermal method. X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM) were used to characterize the Bi₂Se₃ nanoplates, which confirm the single-crystal quality and smooth surface morphology with large size. Micro-Raman spectra over a temperature range of 83–603 K were furthermore used to investigate the lattice dynamics of Bi₂Se₃ nanoplates. Both 2A_g¹ and 1E_g² modes shift evidently with reduced temperature. The line shape demonstrates a significant broadening of full width at half maximum (FWHM) and red-shift of frequency with increased temperature. The temperature coefficient of A_{1g}¹, E_g², A_{1g}² modes were determined to be $-1.258 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, $-1.385 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, $-2.363 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, respectively. Such low temperature coefficient may favor the obtaining of a high figure of merit (ZT) and indicate that Bi₂Se₃ nanoplates were used as excellent candidates of thermoelectric materials.

Keywords: temperature-dependent Raman spectra; temperature coefficient; mode broadening and red-shift; large size Bi₂Se₃ nanoplates

1. Introduction

Recently, 3D layered topological insulators (TIs) materials, such as Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃, have attracted extensive attention due to their unique surface state properties, which are topologically protected against back-scattering and immune to defect-driven localization [1–3]. These materials also are fascinating materials conventionally used in thermoelectricity [4,5]. Thermoelectric materials can be used to directly convert waste heat into electrical power, which is a potential technology for clean and reliable energy harvesting [6]. Improving the energy conversion efficiency is the ultimate goal of global researchers. The record of conversion efficiency was refurbished continuously in the past decade [7,8]. The thermoelectric efficiency is governed by the dimensionless thermoelectric figure of merit ZT ($ZT = S^2 \sigma T / K$, where S , σ , T , and K denote the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively) [9]. Nanostructuring to minimize the thermal conductivity is one of the most common approaches to obtain high ZT [10,11]. For example, nanostructured lead chalcogenides PbQ (Q = Te, Se, S) have demonstrated high thermoelectric ZT [12]. However, Pb-free materials are more desirable to replace the toxic PbQ, which may be unfriendly to the environment and human health.

Raman spectroscopy is a conventional and non-destructive technique for crystal structure characterization [13], which can provide important information on lattice vibration, doping, strain engineering, and crystal phases [14,15]. Insight into the lattice dynamics property is essential to understand the thermal/transport properties, thermal expansion and diffusion, entropy, specific heat, and electron-phonon interaction, all of which have great impact on the thermoelectric performance [16]. Furthermore, it is well known that change of temperature can vary inter-atomic distances and vary the overlap among adjacent electronic orbitals. Therefore, temperature-dependent Raman spectra are well suitable to obtain information on the thermal conductivity of materials, as well as isotopic effects and phonon lifetimes [17–19].

With a band gap of 0.3 eV, Bi_2Se_3 is the most important V–VI semiconductor [20–23]. Bi_2Se_3 has an extensive application as thermoelectric and photoelectric materials near the room temperature [24,25]. Raman spectroscopy was an important tool to characterize the physical properties of various nanostructures, such as: 1T-TaS₂ [26], TiS₃ [27], MoS₂ [28], CoFe₂O₄ [29], CuGaO₂ [30], Bi_{3.25}La_{0.75}Ti₃O₁₂ [31], ZnSe [18,32], ZnO [33], etc. Recently, there are some reports about the Raman-active optical phonon of Bi_2Se_3 micro/nanostructures [34–36]. For example, Zhang et al. reported the synthesis and Raman spectra investigation of few-quintuple layer Bi_2Se_3 nanoplates [37]. However, the size of their Bi_2Se_3 nanoplates was only 0.7–1.6 μm , which makes it hard to obtain the Raman spectra of a single nanoplate under optical microscopy. Therefore, it is highly desired to synthesize large Bi_2Se_3 nanoplates with only a few layers in thickness. As far as we know, there is not yet any report on the Raman spectra of the single solution process Bi_2Se_3 nanoplate. Herein, we synthesized large (7.50–10.0 μm) Bi_2Se_3 hexagonal single-crystal nanoplates by hydrothermal method and investigated their Raman spectra over a wide temperature range of 83–603 K. The variation of Raman peak position and full wave at half maximum (FWHM) with temperature were discussed in detail. The temperature coefficient of A_{1g}^1 , E_g^2 , A_{1g}^2 modes were determined to be $-1.258 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, $-1.385 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, $-2.363 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, respectively. Our results demonstrate that Bi_2Se_3 nanoplates might act as excellent candidates of thermoelectric materials.

2. Experimental Sections

2.1. Preparation of Bi_2Se_3 Nanoplates

All of the reagents used in the experiment were of analytical purity and used without further purification. The typical synthesis procedure is as follows. First, 6 mmol SeO₂, 2 mmol Bi₂O₃, 0.8 g NaOH were dissolved in ethylene glycol (EG). Second, this solution was transferred into a Teflon autoclave, which was heated at 180 °C for 7 h and then cooled to room temperature. The precipitates were centrifuged, washed with distilled water, acetone, and absolute ethanol for several times, and finally dried at 60 °C for 6 h.

2.2. Sample Characterization

Phase identification and structure analysis of the as-obtained sample were carried out by X-ray powder diffraction (XRD, Bruker D8 Advance). The morphology of the final product was characterized by scanning electron microscope (SEM, FEI, NovaSEM-450). The chemical composition and elemental mapping of the sample were analyzed by energy—dispersive X-ray (EDX) spectroscopy. Transmission electron microscope (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) pattern were characterized by TEM (FEI, Tecnai F 20) operating at 200 kV. Raman spectra were measured by high-resolution Raman spectrometer (LabRAM HR Evolution, Horiba JY) using continuous wave (CW) laser with wavelength of 514.5 nm (5 mW excitation power) as excitation light source. The different temperatures were obtained by using Limkam THMS600.

3. Results and Discussion

3.1. Structure and Morphology of Bi_2Se_3 Nanoplates

Figure 1 is the XRD pattern of as-prepared Bi_2Se_3 nanostructures. All the diffraction peaks in the XRD pattern match well with the Bi_2Se_3 rhombohedral lattice phase (JCPDS: 89-2008), and the estimated lattice constants are $a = 0.42$ nm and $c = 2.87$ nm. The six main peaks can be easily indexed to (015), (1,0,10), (1,0,15), (205), (0,2,10) and (1,1,15) planes of Bi_2Se_3 rhombohedral lattice phase [38,39].

Figure 1. XRD pattern of as-prepared Bi_2Se_3 nanostructures.

Figure 2a is SEM image of Bi_2Se_3 nanoplates, which shows the uniform hexagonal morphology in large scale. Figure 2b is low magnification TEM image of single Bi_2Se_3 nanoplate, which has a typical flat surface and sharp edges. These Bi_2Se_3 nanoplates have size of 7.50–10.0 μm , which is large enough to be observed in the optical microscopy for Raman measurement. The SAED pattern shown in Figure 2c exhibits a hexagonal symmetry diffraction spot pattern and indicates the single-crystal nature of Bi_2Se_3 nanoplates. Figure 2d is high-resolution TEM (HRTEM) image [40,41]. The plane spacings were measured to be 0.35 nm. Raman spectrum of single Bi_2Se_3 nanoplate at room temperature is shown in Figure 2e. Three Raman optical phonon modes can be identified as A_{1g}^1 at 68 cm^{-1} , E_g^2 at 127 cm^{-1} , and A_{1g}^2 at 170 cm^{-1} . The peak positions are consistent with the previously measured bulk crystalline Bi_2Se_3 [41].

Hydrothermal method is the chemical reaction in solution at low temperature (below $250\text{ }^\circ\text{C}$). It is a simple while powerful method to obtain desirable crystal materials. By using the hydrothermal method, various structures, include 3D bulk materials, 2D nanoplates, 1D nanowires and 0D nanoparticles, can be synthesized controllable no whether their layer or non-layer nature. The present data indicates that the crystallinity of hydrothermal synthesized Bi_2Se_3 was compared to that of Bridgman method, which was known for the fabrication of single crystal with high crystal quality. Compared with ref 36, we reported the Bi_2Se_3 nanoplates with large size and uniform morphology, which may be used as integrated chip and have potential application in photonics and electronics nanodevices, and our results were based on the single nanoplate that ensured the accurate Raman shift and lattice dynamics.

Figure 2. (a) SEM image. (b) Low magnification TEM image. (c) SAED pattern. (d) HRTEM image. (e) Raman spectrum at room temperature of single Bi₂Se₃ nanoplate.

3.2. Temperature-Dependent Raman Spectroscopy

The rhombohedral crystal structure of Bi₂Se₃ belongs to the $D_{3d}^5(R\bar{3}m)$ space group symmetry. There are five atoms per unit cell in the Bi₂Se₃. This compound contains sandwich structure of the five layers [Se(1)-Bi-Se(2)-Bi-Se(1)], which are held together by van der Waals force. According to the group theory, there are 12 optical modes in Bi₂Se₃. However, four modes ($2A_u^1$ and $2E_u$) are infrared active and can not be observed in the Raman spectrum. So, only eight modes were explained [36,40]. The irreducible representation for the zone-center phonons can be written as [42]:

$$\Gamma = 2E_g + 2A_{1g} + 2E_u + 2A_{1u} \quad (1)$$

It must be noted that the thickness-dependent vibrational frequency of E_g^1 mode is mainly due to the weak van der Waals interlayer interaction. Similar with graphene and MoS₂ [43,44], this mode completely vanishes under single-layer limitation. Here, a , b , and c is a crystal lattice constant of Bi₂Se₃, respectively. The Raman tensor of Bi₂Se₃ are expressed as: [45]

$$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}, E_g = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ d & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -c & d \\ -c & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \quad (2)$$

For temperature-dependent Raman scattering, the Raman spectra were collected by varying the temperature in the range of 83–603 K. As shown in Figure 3a, the intensities of Raman peaks increase significantly with decreased temperature. When the temperature increased from 83 to 603 K, A_{1g}^1 , E_g^2 , and A_{1g}^2 modes are observed to follow a monotonous shift to low wavenumber direction. Such as: the frequency of A_{1g}^1 mode moved from 72 cm^{-1} to 64 cm^{-1} (Figure 3b). The frequency of E_g^2 mode moved from 130 cm^{-1} to 123 cm^{-1} (Figure 3c). The frequency of A_{1g}^2 mode moved from 174 cm^{-1} to 163 cm^{-1} (Figure 3d). We analyzed and discussed the red-shift of Raman peaks and temperature coefficients in Figures 3 and 4. Generally, the research of temperature-dependent Raman spectroscopy is an efficient way to investigate the thermal expansion, thermal conductivity, and interlayer coupling [46,47]. In our experiment, all the Raman peaks had an obvious red-shift with the temperature increasing from 80 to 603 K. In addition, the peak shifts had a linear dependence with the temperature, yielding the first-order temperature coefficient (χ). It has been proposed that

the temperature-dependent peak positions in Raman spectroscopy may result from anharmonicity that results from the thermal expansion and contraction of the crystal and phonon modes [48]. The temperature-dependent line width and intensity could be attributed to the zone-center optical phonon decaying into an optical phonon and an acoustic phonon [48–50].

Figure 3. (a) Raman spectra of Bi₂Se₃ single crystal in the temperature range of 83–603 K. (b–d) A_{1g}, E_{2g}, and A_{1g}² modes of Raman spectra in the temperature range of 83–603 K.

Figure 4a–d plot the peak frequency and FWHM of A_{1g}¹, E_{2g}², and A_{1g}² modes from 83 to 603 K in detail to investigation the temperature effect. The FWHM increased with increase temperature. The peak frequency and FWHM of phonon modes at each temperature can be predicted by theoretical Raman line shape, which can be written as [51]:

$$I(\omega) = \frac{\chi_0 \Gamma_0 \omega \omega_0^2 (\tilde{n} + 1)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma_0^2}, \quad (3)$$

where $\tilde{n} = \exp[\frac{\hbar\chi}{k_B T}] - 1$ is the phonon occupation number, ω_0 and Γ_0 are the peak position and the line width, χ_0 is related with peak intensity, respectively. The peak position and FWHM of these phonon modes at each temperature in our results are consistent with theoretical Raman line shape. The relationship between the peak frequency and temperature was written as [52]:

$$\omega(T) = \omega_0 + \chi T, \quad (4)$$

where ω_0 is the frequency of vibration of these phonon modes at absolute zero temperature, χ is the first-order temperature coefficient of these phonon modes. The evolution of the Raman peak position, ω , follows a linear dependence with the temperature. The different Raman modes χ_i of the first-order temperature coefficients can be fitted linearly. The values of temperature coefficient for each Raman mode are listed in Table 1.

Figure 4. The peak position and temperature (K), FWHM and temperature (K), the peak position and FWHM of A_{1g}^1 (a); E_g^2 (b); A_{1g}^2 (c) Raman active modes in the temperature range of 83–603 K.

Table 1. Comparison of the Raman peak position, FWHM, and temperature coefficient for different Raman modes in the large Bi_2Se_3 hexagonal single-crystal nanoplates.

Raman Mode	Peak Position (cm^{-1})	FWHM (cm^{-1})	χ (cm^{-1}/K)
A_{1g}^1	72	4.83	-1.258×10^{-2}
E_g^2	130	7.06	-1.385×10^{-2}
A_{1g}^2	174	7.30	-2.363×10^{-2}

Figure 4 and Table 1 indicate the temperature evolution for the three Raman modes A_{1g}^1 , E_g^2 , A_{1g}^2 , measured on the Bi_2Se_3 hexagonal single-crystal nanoplates sample. For the Bi_2Se_3 nanoplates, the first order temperature coefficients are $\chi_1 = -1.258 \times 10^{-2} cm^{-1}/K$, $\chi_2 = -1.385 \times 10^{-2} cm^{-1}/K$, $\chi_3 = -2.363 \times 10^{-2} cm^{-1}/K$.

Bi_2Se_3 , a typical thermoelectric material, has temperature evolution of Raman mode further relative to other two-dimensional materials, such as, the transition metal dichalcogenides (TMDCs) (MoS_2 , $MoSe_2$, WS_2 , and WSe_2), black phosphorus, trichalcogenides (TiS_3), which are summarized in Table 2. The calculated χ coefficient was listed in Table 2 and the χ of other materials were summarized

for comparison, indicating the comparable χ coefficient and application of Bi₂Se₃ nanoplates, and thus, our temperature-dependent Raman study can be exploited as large nonlocal signals to measure the temperature in graphene—Bi₂Se₃ heterostructures device [53].

Table 2. The first-order temperature coefficient for the different Raman modes of other two-dimensional materials.

Material	Temperature Coefficient (cm ⁻¹ /K)				Ref
TMDCs	χE_{2g}^1	χA_{1g}	2LA(M)	$A_{1g}(M) + LA(M)$	
MoS ₂ (single layer)	−0.013	−0.016			[54]
MoS ₂ (few-layer)	−0.016	−0.011			[55]
WS ₂ (single layer)	−0.006	−0.006	−0.008	−0.001	[56]
WS ₂ (few-layer)	−0.008	−0.004			[56]
	χA_{1g}	χA_{2U}^2			
MoSe ₂ (single layer)	−0.0054	−0.0086			[57]
MoSe ₂ (few-layer)	−0.0045	−0.0085			[57]
	χE_{2g}^1	χA_{1g}	$A_{1g} + LA$	$2A_{1g}(M) - LA$	
WSe ₂ (single layer)	−0.0048	−0.0032	−0.0067	−0.0067	[57]
black phosphorus	χA_{1g}	χB_{2g}	χA_{2g}		
black phosphorus	−0.008	−0.013	−0.014		[58]
trichalcogenides		χA_{1g}			
TiS ₃ nanoribbons	−0.008	−0.018	−0.021	−0.016	[27]
TiS ₃ nanosheets	−0.022	−0.02	−0.024	−0.017	[27]
dichalcogenides	χA_{1g}^1	χE_{1g}^1	χA_{1g}^2		
Bi ₂ Se ₃ nanoplates	−0.013	−0.014	−0.024		this work

4. Conclusions

In summary, Bi₂Se₃ single-crystal hexagonal nanoplates with size of 7.50–10.0 μm were synthesized successfully at large scale by hydrothermal method. XRD, SEM and TEM show that the as-prepared products have pure phase structure, uniform size distribution and high-quality crystallinity. Temperature-dependent micro-Raman spectra show evident Raman mode shift and FWHM broaden with the temperature range from 83 K to 603 K. The temperature dependence of the vibrational modes of Bi₂Se₃ was found to be almost linear. The temperature coefficient of A_{1g}^1 , E_{2g}^2 , A_{1g}^2 modes were calculated to be $-1.258 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, $-1.385 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, and $-2.363 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, respectively. This low-temperature coefficient is important for obtaining a high figure of merit (ZT). Temperature-dependent Raman study can be exploited as large nonlocal signals to measure the temperature in graphene—a Bi₂Se₃ heterostructures device. The hydrothermal synthesis of large-scale Bi₂Se₃ nanoplates with high performance will push its application in field of thermoelectric materials.

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