Research Article

Synthesis of Novel $\text{Yb}_x\text{Sb}_{2-x}\text{Te}_3$ Hexagonal Nanoplates: Investigation of Their Physical, Structural, and Photocatalytic Properties

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Yb-doped Sb$_2$Te$_3$ nanoplates were synthesized by a coreduction method in hydrothermal condition. Powder X-ray diffraction patterns indicate that the Yb$_x$Sb$_{2-x}$Te$_3$ compounds upon increasing the dopant content ($x$) are isomorphic with Sb$_2$Te$_3$. The cell parameter $a$ decreases for Yb$_x$Sb$_{2-x}$Te$_3$ compounds upon increasing the dopant content ($x$), while $c$ increases. Scanning electron microscopy and transmission electron microscopy images show that doping of Yb$^{3+}$ ions in the lattice of Sb$_2$Te$_3$ produces different morphology. The electrical conductivity of Yb-doped Sb$_2$Te$_3$ is higher than the pure Sb$_2$Te$_3$ and increases with temperature. By increasing concentration of the Yb$^{3+}$ ions, the absorption spectrum of Sb$_2$Te$_3$ shows red shifts and some intensity changes. In addition to the characteristic red emission peaks of Sb$_2$Te$_3$, emission spectra of doped materials show other emission bands originating from $f$-$f$ transitions of the Yb$^{3+}$ ions. The photocatalytic performance of as-synthesized nanoparticles was investigated towards the decolorization of Malachite Green solution under visible light irradiation.

1. Introduction

Antimony telluride ($\text{Sb}_2\text{Te}_3$) based compounds are very promising materials for thermoelectric (TE) applications in solid-state refrigeration and power generation, [1–3] but their extensive application is hindered by their low thermoelectric efficiency. Antimony telluride is a semiconductor with narrow band gap and layered structure. Possessing intrinsically a high figure-of-merit (ZT) because of its large Seebeck coefficient, this compound and its doped derivatives are considered to be the best candidates for near room-temperature TE applications [4–7]. Rare earth ions doped nanomaterials have become an increasingly important research topic and opened up the opportunity for creating new applications in diverse areas, such as light emitting displays, biological labeling, and imaging [8–10]. Investigations of impurity effects or doping agents on the physical properties of Sb$_2$Te$_3$ are attractive both for applied and basic research. Incorporating trivalent cations such as Sb$^{3+}$ [11], ln$^{3+}$ [12], Fe$^{3+}$ [13], Mn$^{3+}$ [14], and some trivalent 3d elements [15] to the lattice of Bi$_2$Se$_3$ has been reported. Also, Ln$_x$Bi$_{2-x}$Se$_3$ (Ln: Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, and Nd$^{3+}$) based nanomaterials were prepared by Alemi et al. [16, 17]. Recently, we have synthesized new luminescent nanomaterials based on doping of lanthanide (Ln: Ho$^{3+}$, Nd$^{3+}$, and Lu$^{3+}$) into the lattice of Sb$_2$S$_3$ and (Ln: Ho$^{3+}$, Nd$^{3+}$, Lu$^{3+}$, Sm$^{3+}$, Er$^{3+}$, and Yb$^{3+}$) into the lattice of Sb$_2$Se$_3$ [18–21]. To the best of our knowledge, there is no study about doping of rare earth cations into the lattice of Sb$_2$Te$_3$. The electronic properties of antimony telluride could be affected by doping of lanthanide ions into a Sb–Te framework. Herein, we report synthesis of Yb$_x$Sb$_{2-x}$Te$_3$ nanomaterials by a hydrothermal route. Structural and spectroscopic properties and electrical and thermal conductivity of the as-prepared materials are described. Also, the photocatalytic activity of Yb$_x$Sb$_{2-x}$Te$_3$ nanomaterials was investigated towards Malachite Green (as a model organic dye) decolorization under visible light irradiation.

2. Experimental

All chemicals were of analytical grade and were used without further purification. Tellurium powder, Sodium Borohydride,
SbCl₃, Yb₂O₃, NaOH, and Malachite Green were obtained from Merck. The characteristic of this dye is presented in Table 1. Ethanol (99%). 4H₂O were obtained from Aldrich.

3. Synthesis of Sb₂Te₃ and Yb-Doped Sb₂Te₃ Samples

Tellurium powder (0.382 g) and NaOH (0.6 g) were added to distilled water (60 mL) and stirred well for 10 min at room temperature. Afterwards, Sodium Borohydride (4 g), SbCl₃, and Yb₂O₃ with appropriate ratios were added, and the mixture was transferred to a 100 mL Teflon-lined autoclave. The autoclave was sealed, maintained at 180°C for 48 h, and then allowed to cool to room temperature naturally. The as-synthesized YbₓSb₂⁻ₓTe₃ nanomaterials were collected and washed with distilled water and absolute ethanol several times in order to remove residual impurities and then dried at room temperature. The final black powders were obtained as a result.

4. Characterization Methods

The products yields were 85–95%. X-ray powder diffractometer (XRD D5000 Siemens AG, Munich, Germany) with CuKα radiation was used for phase identification. The morphology of the materials was examined using a JEOL JSM-6700F Scanning Electron Microscope (SEM). A linked ISIS-300, Oxford EDS (energy dispersion spectroscopy) detector was used for elemental analyses. The SAED pattern and HRTEM image were performed by a Cs-corrected high-resolution TEM (JEM-2200FS, JEOL) operated at 200 kV.
Figure 3: The SEM image (a) and EDX (b) of as-prepared Sb$_2$Te$_3$ synthesized at 180°C and 48 h.

Figure 4: The SEM image (a and b), TEM image (c), and SAED pattern (d) of as-prepared Yb$_{0.02}$Sb$_{1.98}$Te$_3$ nanoplates at different magnifications synthesized at 180°C and 48 h.

Photoluminescence measurements were carried out using a Spex FluoroMax-3 spectrometer. The absorption spectra were recorded with UV-Vis spectrophotometer (Varian Cary 3 Bio). The UV-Vis diffuse reflectance spectra were used for evaluation of photophysical properties of as-synthesized material. The electrical and thermoelectrical resistivity of samples was measured by Four Probe Method. An oven was required for the variation of temperature of the samples from the room temperature to about 200°C. Small chip with 1 mm thickness and 7 mm length was used for this analysis. This
chip was obtained by pressing of 30 mg of sample under 30 kpa pressing device. Celref program (CCP14, London, UK) and WinXPOW program (STOE & CIE GmbH, Darmstadt, Germany) using a profile fitting procedure were used for calculation of cell parameters from powder XRD patterns and determination of reflections, respectively.

5. Photocatalytic Studies

The photocatalytic activity of undoped and Yb$_{x}$Sb$_{2-x}$Te$_3$ nanomaterials was evaluated by the decolorization of Malachite Green (a triphenylmethane dye) in an aqueous solution under visible light. In a typical process, 0.1 g of the photocatalyst powder was added to 100 mL Malachite Green solution...
with an initial concentration of 5 mg/L. The suspension of photocatalyst and Malachite Green was magnetically stirred in a quartz photoreactor in the dark for 15 mins to establish an adsorption/desorption equilibrium of the dye. Then, the solution was irradiated by a 6 W fluorescent visible lamp (GK-140, China) as the light source. The color removal efficiency (CR (%)) was expressed as the percentage ratio of decolorized dye concentration to that of the initial one. During the photocatalytic process, 5 mL of the suspension was sampled at desired times and after centrifugation, the removal of color was evaluated by determining the absorbance of the solution at \( \lambda_{\text{max}} = 619 \) nm by using UV-Vis spectrophotometer, Lightwave S2000 (England).

6. Results and Discussion

The lattice parameters were determined via reflections observed in \( 2\theta = 4^\circ - 70^\circ \). An X-ray diffraction (XRD) pattern of the newly obtained Yb-doped Sb\(_2\)Te\(_3\) is shown in Figure 1(a). All peaks can be perfectly indexed to rhombohedral Sb\(_2\)Te\(_3\) (space group: R-3m) with lattice constants \( a = 4.264 \text{ Å} \) and \( c = 30.458 \text{ Å} \) (Joint Committee on Powder Diffraction Standards (JCPDS) card number 15-0874). Additional unknown phases as shown by stars in Figure 1(b) were observed beyond doping levels of \( x = 0.05 \) for Yb\(^{3+}\).

The calculation of cell parameters of the as-prepared materials was done from the XRD patterns. By increasing dopant content \( (x) \), the \( a \) parameter for Yb\(^{3+}\) decreases, while the \( c \) parameter increases, as shown in Figure 2. These changes of lattice constants can be attributed to the effective ionic radii of the Yb\(^{3+}\) ions and lattice shifts to various position of dopants or defects site. Figure 3 shows SEM image and EDX of Sb\(_2\)Te\(_3\) nanoparticles. The thickness of these plates is around 40–80 nm. The EDX analysis of the product confirms the ratio of Sb/Te to be 2:3, as expected. Doping of various Yb\(^{3+}\) concentrations into the structure of Sb\(_2\)Te\(_3\) results in different morphology. At lower Yb\(^{3+}\) composition the morphology is hexagonal nanoplate as seen in Figure 4 in which the thickness of plates is around 40–90 nm and at higher Yb\(^{3+}\) concentration the product is nanoparticles. Figure 4 shows SEM, TEM image, and SAED pattern of Yb\(_{0.05}\)Sb\(_{1.95}\)Te\(_3\) nanoparticles whose diameter is around 20–50 nm. The TEM image and SAED pattern of Yb\(_{0.02}\)Sb\(_{1.98}\)Te\(_3\) confirm the result of SEM and shows crystallinity of product as seen at Figure 5. As expected, the EDX analysis of the product confirms purity and the ratio of Sb/Te/Yb (see Figure 6). The electronic properties of antimony telluride could be affected by doping of lanthanide ions into a Sb–Te framework. Doping of lanthanide cations into Sb\(_2\)Te\(_3\) lattice results in decreasing the Sb–Te covalence bond. Due to different interaction in the doped Sb\(_2\)Te\(_3\) lattice, there are different growth directions in lattice and production of various morphologies. The Four Probe Method was used for the measurement of electrical and thermoelectrical resistivity.
of samples (Figure 7). Figure 8(a) shows electrical resistivity of Yb-doped Sb$_2$Te$_3$ nanomaterials. The electrical resistivity measured at room temperature for pure Sb$_2$Te$_3$ was of the order of 0.09 Ω·m. The minimum value of electrical resistivity for Yb$^{3+}$-doped compounds is 0.0081 Ω·m. Figure 8(b) shows the temperature dependence of the electrical resistivity for Yb-doped Sb$_2$Te$_3$ between 290 and 340 K in which the electrical resistivity decreases with temperature. The minimum value of electrical resistivity for Yb$_{0.05}$Sb$_{1.95}$Te$_3$ is 0.0007 Ω·m. As a result, the electrical conductivity of Yb-doped Sb$_2$Te$_3$ materials is higher than undoped Sb$_2$Te$_3$ at room temperature and increases with temperature. Selected absorption spectra of Sb$_{2−x}$Yb$_x$Te$_3$ (x = 0.02 and 0.05) are shown in Figure 9. The DRS spectra of Sb$_2$Te$_3$ lattice show an intensive peak around 480 nm. The absorption spectra in the spectral region 800–900 nm can be assigned to electronic transitions of Yb$^{3+}$ from the $^2F_{7/2}$ ground state to $^2F_{5/2}$ excited level [22, 23]. As shown in Figure 9, there is a red shift in DRS spectra of Sb$_{2−x}$Yb$_x$Te$_3$ compounds, respectively. The calculated band gaps from absorbance spectra for Sb$_{2−x}$Yb$_x$Te$_3$ are $E_g = 2.587$ eV (Yb-0.02) and 2.48 eV (Yb-0.05). Figure 10 exhibits the RT PL emission spectra of Sb$_{2−x}$Yb$_x$Te$_3$ compounds. Two peaks are shown in the PL spectra of Yb$^{3+}$-doped compounds attributed to Sb$_{2}$Te$_3$ lattice centered at 560 nm and another is assigned to f-f transitions of Yb$^{3+}$ ions from $^2F_{5/2} \rightarrow ^2F_{7/2}$. There are red shifts in PL spectra by increasing concentration of Yb$^{3+}$ [22, 23]. Figure 11 shows the typical evolution of the absorption spectra of C.I. Basic Green-4 under the irradiation of visible light using the Yb$_{0.05}$Sb$_{1.95}$Te$_3$ nanoparticles as a photocatalyst. The absorption peak around 355 nm gradually weakened and decreased from the absorption spectra, indicating the degradation of the BG4. The loss of absorbance may be due to the destruction of theazo bond and dye chromogen. Since no new peak was observed, the BG4 has been decomposed. Also, the photocatalytic activity of synthesized undoped and Yb-doped Sb$_2$Te$_3$ nanoparticles was compared and is presented in Figure 12. In a typical process, 100 mL of BG4 (5 mg/L) aqueous solution and 0.1 g of photocatalyst powder were mixed in a quartz photoreactor. It is clearly seen from Figure 12 that the color removal efficiency of the Yb-doped Sb$_2$Te$_3$ catalyst is much higher than that of pure Sb$_2$Te$_3$. The results demonstrated the good photocatalytic ability of these nanoparticles under visible light and can be compared with other new catalysts [24–26]. As can be seen, the decolorization efficiency is 16.30 and 75.62% after 120 min of treatment for Sb$_2$Te$_3$ and Yb$_{0.05}$Sb$_{1.95}$Te$_3$, respectively.

7. Conclusion

Novel thermoelectric Yb$_x$Sb$_{2−x}$Te$_3$ based nanomaterials were synthesized by a simple and efficient coreduction method at 48 h and 180°C at basic media. According to SEM and TEM images, different morphologies were seen in Yb-doped...
Sb$_2$Te$_3$. Lanthaneide doping promotes the electrical conductivity of Sb$_2$Te$_3$ as well as thermal conductivity. UV-Vis absorption and emission spectroscopy reveals mainly electronic transitions of the Yb$^{3+}$ doping nanomaterials. Red shifts as well as increasing of intensity of absorption and emission peaks were seen in doped nanomaterial. Experiments showed that the as-obtained nanoparticles have high photocatalytic activity under visible light irradiation. The decolorization efficiency of BG4 solution using these photocatalysts was 16.30 and 75.62% after 120 min of treatment for Sb$_2$Te$_3$ and Yb$_{0.05}$Sb$_{1.95}$Te$_3$, respectively.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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**References**


