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Study on effects of sodium hydroxide on synthesis of zinc telluride nanocrystals by hydrothermal method

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ABSTRACT

Zinc telluride nanocrystals were synthesized in sodium hydroxide solution by the hydrothermal method using zinc and tellurium powders. The zinc telluride nanocrystals were analyzed by X-ray diffractometry, transmission electron microscopy and micro-Raman spectroscopy. The X-ray diffraction patterns indicate that zinc telluride crystallizes in zincblende structure and the residual impurities change with the content of sodium hydroxide. The images of transmission electron microscopy show that the size of zinc telluride nanocrystals varies with the content of sodium hydroxide. The Raman spectra exhibit a series of longitudinal optical multiphonon peaks up to the fourth order peak. Employing theory related to crystal growth and resonance Raman scattering, growth of zinc telluride nanocrystals was studied and their band gaps were estimated. These results lead to further insights into controlling the synthesis of zinc telluride nanocrystals and correlation with their electronic structure.

1. Introduction

II–VI compound nanomaterials have been extensively studied due to their interesting properties and potential applications in the field of solid devices [1–3]. In particular, zinc telluride (ZnTe) nanomaterials have attracted much attention in recent years. ZnTe is a direct wide band gap II–VI semiconductor materials with a band gap of 2.26 eV at 300 K. ZnTe nanomaterials have many potential applications in nanoscale electronic and optoelectronic devices owing to their remarkable physical properties [4]. For example, the ZnTe nanowires have been used to fabricate the nanoscale field-effect transistors and photodetectors [4–6]. To date, various methods were used to synthesize the ZnTe nanostructures, such as ZnTe nanocrystals by microwave plasma [7], ZnTe nanorods by hydrothermal method [8] and ZnTe nanowires by thermal evaporation and molecular beam epitaxy [9,10]. In previous work, we studied hydrothermal synthesis of ZnSe nanocrystals and Raman scattering from them [11,12]. In this work, we reported studies on the growth of ZnTe nanocrystals in sodium hydroxide (NaOH) solution and the Raman scattering from them. It is found that the growth of the ZnTe nanocrystals was related to the NaOH content in the solution. In addition, the resonant Raman scattering was observed. Employing theory related to crystal growth and resonance Raman scattering, growth of zinc telluride nanocrystals was studied and their band gaps were estimated.

2. Experimental details

The ZnTe nanocrystals were synthesized in NaOH solution by the hydrothermal method described in Ref. [11]. A definite content of zinc, tellurium and sodium hydroxide powders were mixed in a Teflon-lined autoclave of 50 mL capacity and the deionized water was poured into the

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Table 1
Content of Zn, Te, NaOH powders, the growth temperature T_g and time t_g.

Sample	Zn (g)	Te (g)	NaOH (g)	T_g (°C)	t_g (h)
A	0.67	1.32	6.43	120	2
B	0.67	1.32	3.22	120	2
C	0.67	1.32	1.60	120	2

Teflon liner up to 80% of the capacity. The autoclave was sealed into a stainless steel tank and heated at a rate of 5 °C/min and kept at a constant reaction temperature for several hours in an oven. After the oven was cooled to room temperature, the products were collected by centrifugal sedimentation and washed with deionized water repeatedly. Finally, they were dried at 70 °C for 8 h to get purple powders. In the experiment, three samples A–C were prepared, and the growth conditions are listed in Table 1. Among these conditions, the content of NaOH powder is successively reduced from A to C samples, and other conditions are kept unchanged.

The phases of the ZnTe nanocrystals were analyzed by a Bruker D-8 Advance X-ray diffractometer (XRD) using Cu Kα radiation. The morphologies of the ZnTe nanocrystals were observed by a Philips Tecnai-12 transmission electron microscopy (TEM) (operated at 120 KV). To further confirm the crystal structure of the ZnTe crystals, the electron diffraction pattern should be obtained. However, it is difficult to obtain the electron diffraction pattern of a single ZnTe particle using the Philips Tecnai-12 TEM due to the aggregation of the ZnTe nanocrystals, thus the sample A was observed by a FEI TECNAI G^2 TEM again (operated at 200 kV) to obtain the electron diffraction pattern of a single ZnTe particle by selecting a ZnTe particle near the edge of the aggregated ZnTe nanocrystals. The samples for TEM images were prepared by suspending the ZnTe powder in ethanol. About 1–2 mg of the ZnTe powder was added to 5 mL of ethanol in a small glass vial, followed by ultrasonic separation for 5 min. Few drops of the suspension were added onto a carbon-coated 100 mesh copper grid and dried under ambient condition before imaging. The Raman spectra were recorded at room temperature by Renishaw micro-Raman spectroscopy in which an Ar-ion laser at 514 nm was used as the excitation sources.

3. Results

Fig. 1 shows the XRD spectra of the A–C samples. In Fig. 1, the diffraction peaks at about $2\theta=25.2°$, 41.8°, 49.5° and 66.9° are indexed to ZnTe crystals (JCPDS 65-0385) and confirm that the ZnTe nanocrystals crystallizes in zincblende structure [9]. The peaks at about $2\theta=23.0°$, 27.5°, 38.3° and 40.4° are from the diffraction of tellurium crystal (JCPDS 65-3370). The other peaks at about $2\theta=36.3°$, 43.2° and 54.3° result from the diffraction of zinc crystal (JCPDS 65-3358). Compared with the intensities of the peaks related to tellurium and zinc, it can be known that the residual zinc and tellurium in the A–C

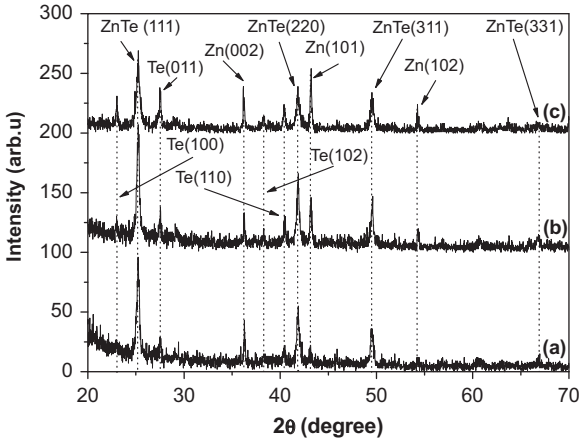

Fig. 1. XRD spectra of the ZnTe nanocrystals grown under different NaOH contents in the NaOH solution: (a) 6.43 g, (b) 3.22 g and (c) 1.60 g.

Table 2
θ, β_{in}, β_s and β_f valves of the (111) peak, and the d values of the samples.

Sample	θ (deg.)	β_{in} (deg.)	β_s (deg.)	β_f (arc)	d (nm)
A	12.6	0.18	0.26	0.0033	43
B	12.6	0.18	0.28	0.0037	38
C	12.6	0.18	0.33	0.0049	29

samples are gradually enhanced in turn. According to Scherrer's formula, the sizes of the ZnTe crystals can be estimated. The formula is

$$d=\frac{k\lambda}{\beta\cos\theta}, \tag{1}$$

where d is the size, k is the geometric factor, which usually takes a value of 0.9, λ is the wavelength of Cu Kα radiation (0.15406 nm) and β and θ are the full width at half maximum (FWHM) of the diffraction peak and Bragg's angle, respectively [7]. As shown in Fig. 1, the (111) peak is the strongest; thus the sizes are estimated by the (111) peak [7]. From Fig. 1, the FWHM values of the (111) peak in the spectra (a)–(c) are obtained and they are shown in Table 2. Due to existence of the FWHM produced by instrument, the factual FWHM is obtained by

$$\beta_f=\sqrt{\beta_s^2-\beta_{in}^2}, \tag{2}$$

where β_f, β_s and β_{in} are the factual, spectrum and instrument FWHM values [13], respectively. By Eq. (2), we obtain the β_f values, and then get the average sizes of the ZnTe nanocrystals by Eq. (1), which are given in Table 2.

Fig. 2 is the Raman spectra of the A–C samples. All the spectra show three scattering peaks at about 205, 409 and 614 cm^{-1}, which are attributed to the first order longitudinal optical (1LO), 2LO and 3LO phonon modes of ZnTe crystal, respectively [7]. In addition, the spectra (a) and (b) show the scattering peaks at about 268 and 819 cm^{-1}, which are related to the Raman scattering from tellurium [9] and the 4LO phonons in ZnTe crystal [14], respectively.