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CHARACTERIZATION AND PHOTOLUMINESCENCE OF PbS NANOCUBES SYNTHESIZED BY A SOLVOTHERMAL METHOD

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PbS nanocubes were synthesized by a solvothermal method using $PbCl_2$ and NH_2CSNH_2 as a starting agents in 1,2-propadiol as a solvent at 100-200 ^oC for 10-30 h. The PbS nanocubes were analyzed using an X-ray diffraction, a Raman spectroscopy, a transmission electron microscopy and a photoluminescence spectrometry. The photoluminescence property was influenced by the reaction temperatures and times.

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1. Introduction

In recent years, the calcogenides are very interesting semiconductors because of their potential applications: such as sensors, lasers, catalytic materials, and IR detectors. One of them is PbS, which has a small band gap (0.41 eV) and large exciton Bohr radius (18 nm) [1-3]. PbS has been synthesized to achieve various morphologies such as star-like [4], fish bone-like [1], flower-like [2,3] and nano-dendrite [1]. Their different morphologies play a role in determining their properties [5]. In 2007, Cao et al. [6] reported the preparation of PbS nanocubes by hydrothermal method using lead acetate hydrate and dithioglycol as starting materials without any surfactant adding in absolute ethanol at 220 ^oC for 4 h. In this manuscript, the synthesis of PbS nanocubes by solvothermal method with no addition of surfactants, capping agents and templates was reported in order to specify its photoluminescence property.

2. Experimental procedure

The PbS nanocubes were prepared using lead chloride ($PbCl_2$) and thiourea (NH_2CSNH_2) as material sources in propadiol as a solvent. First, each 0.005 mole of $PbCl_2$ and NH_2CSNH_2 was dissolved in 15 ml 1,2-propadiol solution. Then they were mixed together, under stirring for 30 min at room temperature. The solution was transferred into a Teflon-lined autoclave, which was sealed, heated to 100-200 ^oC for 10-30 h, and cooled down to room temperature. The products were collected, and washed with deionized water and 95 % ethanol, and dried at 80 ^oC for 12 h – for further characterization using X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), and photoluminescence spectrometry.

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3. Results and discussion

XRD spectra in Fig. 1a corresponded with the JCPDS database no. 05-0592 for cubic PbS [7]. The intensities of their peaks are very high and sharp, corresponding to the high crystalline products. Their lattice parameters were calculated form the equation of plane spacing for the cubic crystal system and Bragg's law for diffraction [8]. For the product prepared by 200 ^{o}C and 10 h solvothermal reaction, its lattice parameter is 5.9375 Å. It was very close to that of the JCPDS database no. 05-0592 [7]. The crystallite sizes of these products were calculated using Scherrer's equation [8], $B = \lambda k/L\cos\Theta$, w here λ is the wavelength of Cu Kα radiation (0.15406 nm),Θ the Bragg angle, L the average crystallite size, k a constant (k = 0.89), and B the full width at half maximum in radian unit. Crystallite sizes of the products prepared at 100 ^{o}C for 10 h, 100 ^{o}C for 30 h, and 200 ^{o}C for 10 h were 20.30, 24.96, and 35.28 nm, respectively. It should be noted that the crystalline degree and crystallite size of the products were influenced by the prolonged holding time and the high temperature increase.

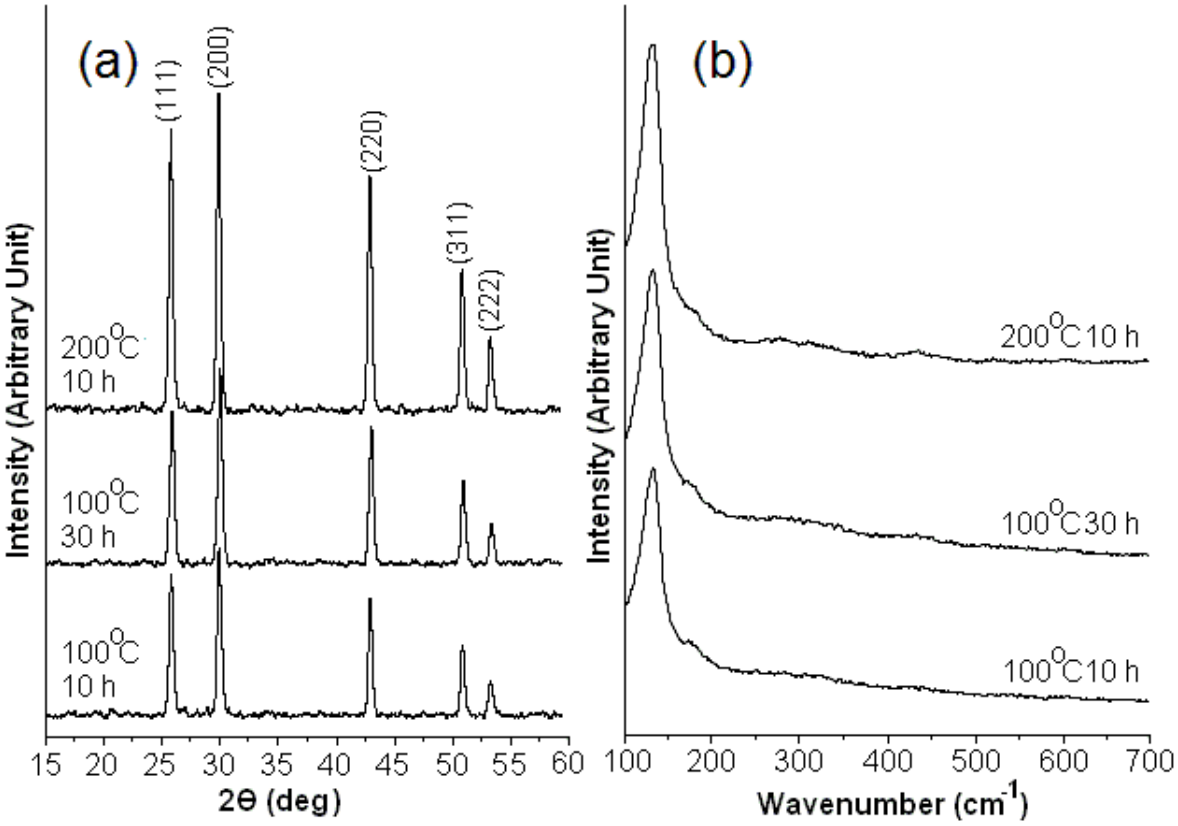

Fig. 1 XRD patterns and Raman spectra of PbS prepared by a solvothermal reaction at different conditions.

The 514.5 nm wavelength Ar laser for Raman spectroscopy was used to analyze the products. The spectra for different conditions displayed in Fig. 1b show the same wavenumber at 135, 217, 433 and 649 cm^{-1}. The 217, 433 and 649 cm^{-1} peaks corresponded to the fundamental longitudinal optical (LO) phonon mode of rock-salt structure, first overtone (2LO) and second overtones (3LO), respectively. The strong band at 135 cm^{-1} is attributed to a combination of longitudinal and transverse acoustic modes. However, the positions and intensities of the Raman peaks were also influenced by the difference in particle sizes, excitation wavelengths, and temperatures [2,3,6].

TEM image and SAED pattern of PbS nanocubes prepared by the solvothermal method at 200 ^{o}C for 10 h are shown in Fig. 2. The TEM image presents nanocube structure with the length

and width of about 100 and 50 nm. The SAED pattern shows a number of randomly and continuously bright spots, which are so close that they formed several fully concentric rings. These indicate that the product was consisted of nano-sized crystals with different orientations. Calculated interplanar spaces were compared with those of the JCPDS database no. 05-0592 [7]. They correspond to the (111), (200), (220), (311), (222), (400) and (331) planes of the cubic PbS structure.

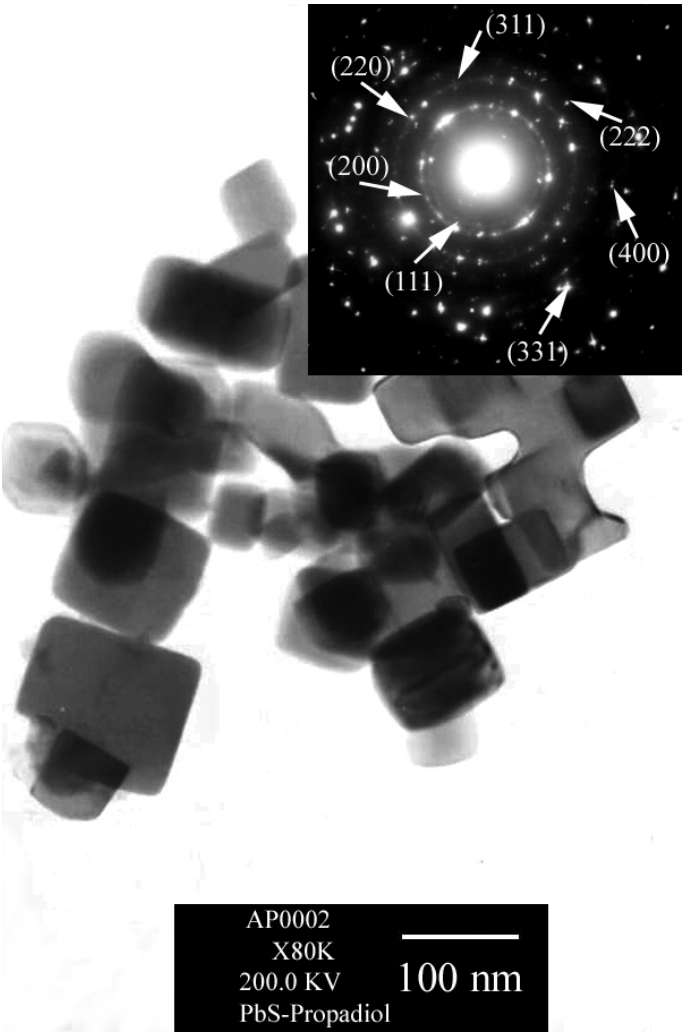

Fig. 2 TEM image and SAED pattern of PbS, prepared by the 200 ^{o}C and 10 h solvothermal method.

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A possible formation mechanism of PbS nanocubes is able to be expressed as follows:

$$NH_2CSNH_2 + H_2O \rightarrow NH_2CONH_2 + H_2S \quad (1)$$

$$Pb^{2+} + S^{2-} \rightarrow PbS \quad (2)$$

H_2S was generated by the hydrolysis of thiourea by H_2O. Subsequently, H_2S reacted with Pb^{2+} to synthesize PbS nuclei [1]. As time passed, the PbS nuclei concentration increased, and grew and arranged themselves to be a cubic structure, controlled by the surface energy effect. When the PbS nuclei has higher growth rate in the [111] direction than those in other directions [1,4], the PbS nanocubes would be achieved.

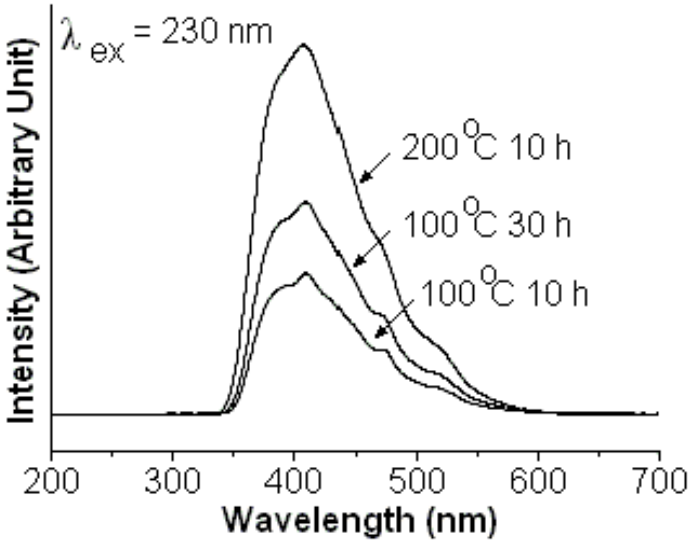

Fig. 3 Photoluminescence spectra of PbS, prepared by the 200 ^{o}C and 10 h solvothermal method.

Photoluminescence (PL) property of the products, excited by the 230 nm wavelength (λ_{ex}), is shown in Fig. 3. The maximum intensities were detected at the same wavelength of 422 nm, in accordance with the previous reports [5,6]. Their intensities were increased with the increase in the solvothermal temperatures and reaction times. In general, the intensities are very sensitive to the crystalline degree of the products.

4. Conclusions

PbS nanocubes were successfully synthesized by the solvothermal method. The crystallinity and photoluminescence property of the products were increased with the increase in the solvothermal temperatures and times. The PbS nanocubes show the highest emission intensity peak at 422 nm.

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