



# Synthesis and photoluminescence properties of aqueous CdWO<sub>4</sub> quantum dots with WO<sub>6</sub><sup>6-</sup> luminescence center

Guoxin Zhang<sup>a,\*</sup>, Sefei Yang<sup>b</sup>, Zheng Li<sup>a</sup>, Lan Zhang<sup>a</sup>, Wei Zhou<sup>a</sup>, Haiying Zhang<sup>c</sup>, Hua Shen<sup>a</sup>, Yongxian Wang<sup>a</sup>

<sup>a</sup> Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 2019 JiaLuo Road, Shanghai 201800, China

<sup>b</sup> Department of Stomatology, The Chinese PLA General Hospital, Beijing 100853, China

<sup>c</sup> Department of Chemical Engineering, Shanghai Institute of Technology, Shanghai 200235, China

## ARTICLE INFO

### Article history:

Received 8 January 2010

Received in revised form 6 May 2010

Accepted 1 July 2010

Available online 7 July 2010

### Keywords:

CdWO<sub>4</sub>

Quantum dots

Photoluminescence

WO<sub>6</sub><sup>6-</sup> luminescence center

Synthesis mechanism

## ABSTRACT

Aqueous CdWO<sub>4</sub> QDs were synthesized by the reaction of CdCl<sub>2</sub> and Na<sub>2</sub>WO<sub>4</sub> in the presence of mercaptoacetic acid (TGA) as capping reagent. The crystal morphology, particle size and its distribution of as-prepared products were characterized by transmission electron microscopy (TEM, SAED) atomic force microscopy (AFM), high-resolution transmission electron microscopy (HRTEM), and photon correlation spectroscopy (PCS), respectively. Qualitative assays for functional groups on the QDs' surface were measured by fourier transform infrared spectroscopy (FTIR). Photoluminescence properties of QDs were studied by photoluminescence spectroscopy (PL). The results showed that the single QD with diameter of about 8 ± 2 nm was single-crystal. The particle size distribution of QDs was normal. Infrared absorption bands of carboxylic group on the surface of CdWO<sub>4</sub> QDs were observed around 1610–1550 cm<sup>-1</sup> (non-symmetrical vibration of -COO<sup>-</sup>) and 1400 cm<sup>-1</sup> (symmetric vibration of C–O). With reaction-time going, PL peak position shifted from 498 to 549 nm and intensity of PL increased first and then decreased. PL peak position of QDs was blue-shift compared with 570 nm WO<sub>6</sub><sup>6-</sup> luminescence center of bulk CdWO<sub>4</sub>.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Quantum dots (QDs) have attracted intense attention because of their many desirable properties, such as a wide absorption band, strong emission, and their durability when exposed to light irradiation [1]. QDs with above-mentioned characteristics can be applied into the fields of biochemistry [2–4], optoelectronics [5,6], etc. These properties depend strongly on the particle size as a consequence of their quantum confinement, coming from the changes in density of their electronic states [7]. That is to say, QDs' optical properties can be adjusted by controlling their size.

QDs are thought generally to be formed by atoms from group II (alkali metals, metal oxides or organic salts) and group VI (Se, S and Te) [8]. And lots of studies focus on these II–VI semiconductor QDs. However, there are no reports on properties of QDs prepared by oxysalt so far. Especially, oxysalt with luminescence center should be paid attention so as to further reveal their optical properties. Tungstates as oxysalt have attracted much interest because of their

approved use as scintillating medium and in electro-optic applications (i.e. solid-state laser and in optical fibre applications) [9–11]. Nano-scale can make tungstates increase their light yield to extend their application [12]. Therefore, it is distinct that the tungstates QDs have promising optical properties.

Cadmium tungstate (CdWO<sub>4</sub>) nanocrystals with monoclinic symmetry (C<sub>2h</sub><sup>4</sup>) are interesting because of their high average refractive index, low radiation damage, low afterglow, high X-ray absorption coefficient [13], and luminescence property [14]. They can be used, for instance, as an X-ray scintillator [15,16] and laser materials. Concerning luminescence property, intrinsic luminescence in CdWO<sub>4</sub> crystals originates from tungstate groups of these crystals. According to generally accepted view, the centers of luminescence in CdWO<sub>4</sub> crystals are in some or other way related to the tungstate groups WO<sub>6</sub><sup>6-</sup> of these crystals. (It consists of Cd cations and tungstate groups in the anionic positions. Each tungsten atom has six oxygen atoms in the nearest surroundings forming distorted octahedral tungstate groups WO<sub>6</sub><sup>6-</sup> [17].)

In this work, experiments proved that the CdWO<sub>4</sub> QDs with excitation Bohr radius could be synthesized by aqueous phase modified-method. In addition, CdWO<sub>4</sub> QDs' synthesis mechanism was brought forward also. The photoluminescence (PL) properties of CdWO<sub>4</sub> QDs with WO<sub>6</sub><sup>6-</sup> luminescence center were studied as reaction time went along.

\* Corresponding author. Tel.: +86 21 39194695; fax: +86 21 39194696.

E-mail address: [zhangguoxin@sinap.ac.cn](mailto:zhangguoxin@sinap.ac.cn) (G. Zhang).

## 2. Experiment

### 2.1. Reagents

Absolute ethanol ( $C_2H_5OH$ ), mercaptoacetic acid (TGA,  $HSCH_2COOH$ ), sodium hydroxide (NaOH), cadmium chloride ( $CdCl_2$ ) and sodium tungstate ( $Na_2WO_4$ ) were all analytically pure. The above reagents were purchased from Shanghai Chemical Reagents Co. Ltd. Milli-Q water (ultrapure water) was obtained from Milli-Q plus system (Millipore, Molsheim, France) was deoxygenated prior to use.

### 2.2. Synthesis of $CdWO_4$ QDs

Based on the literature [18] and our previous works [19], the  $CdWO_4$  QDs were prepared by aqueous phase modified-method. Solution A: 20  $\mu$ l TGA was added into 100 ml 0.001 mol/l  $CdCl_2$  to form grey cloudy solution, pH value of which was adjusted to 9.0 by NaOH (0.1 mol/l). And cloudy solution was changed into clarification when pH value was 7; solution B: 0.05 mmol  $Na_2WO_4$  was dissolved in Milli-Q water. Solution B was added to the solution A drop by drop, when solution A was heated to 100 °C with stirring, reflux and  $N_2$  protection. Then the mixed solution was cooled down to the room temperature. Evaporation was carried out to concentrate the solution by rotating at 45 °C under vacuum. And the volumes of concentrated solution should be remained above 10 ml. Then, the final  $CdWO_4$  products were collected by centrifugation at the speed of 12000 rpm.

### 2.3. Characterization of sample

(1) As-prepared  $CdWO_4$  QDs collected after reaction time of 4 h were put on the copper mesh, the morphology and size of which

were observed by Transmission Electron Microscopy with an accelerating voltage of 200 kV (TEM, Hitachi, H-800, Japan). And the electron diffraction pattern of the  $CdWO_4$  QDs was obtained by SAED (Selected Area Electron Diffraction) of TEM. The sample also was detected by High-Resolution Transmission Electron Microscopy (HRTEM, JEOL, JSM-2010F, Japan). In addition, the morphologies of  $CdWO_4$  QDs which were put on the mica substrate were also evaluated by Atomic Force Microscopy (AFM, SEIKO, SPA-400, Japan).

- (2) The photoluminescence properties of  $CdWO_4$  QDs collected at every half hour from the reaction beginning were ready to measure. The photoluminescence properties were characterized by Photoluminescence Spectrophotometer (PL, Hitachi, F-4500, Japan). The PMT voltage was 700 V and scan speed was 2400 nm/min. The excitation wavelengths were at 330, 340, 350, 360, 370 and 380 nm, respectively.
- (3) In this experiment, the concentration of  $CdWO_4$  QDs collected after reaction time of 4 h was diluted using Milli-Q water to 0.005% and was tested by Photon Correlation Spectroscopy (PCS, Malvern, Zetasizer Nano S, England).
- (4) The final  $CdWO_4$  products were measured by the Nicolet NEXUS870 FT-IR spectrometer (IR, USA).

## 3. Results and discussion

### 3.1. Morphology and size analysis

Fig. 1 was the TEM, AFM and HRTEM picture of as-prepared samples collected after reaction time of 4 h. AFM pattern (Fig. 1B) illustrated that as-prepared products presented monodisperse. In the TEM and HRTEM (Fig. 1A and C), the particle's diameter was of

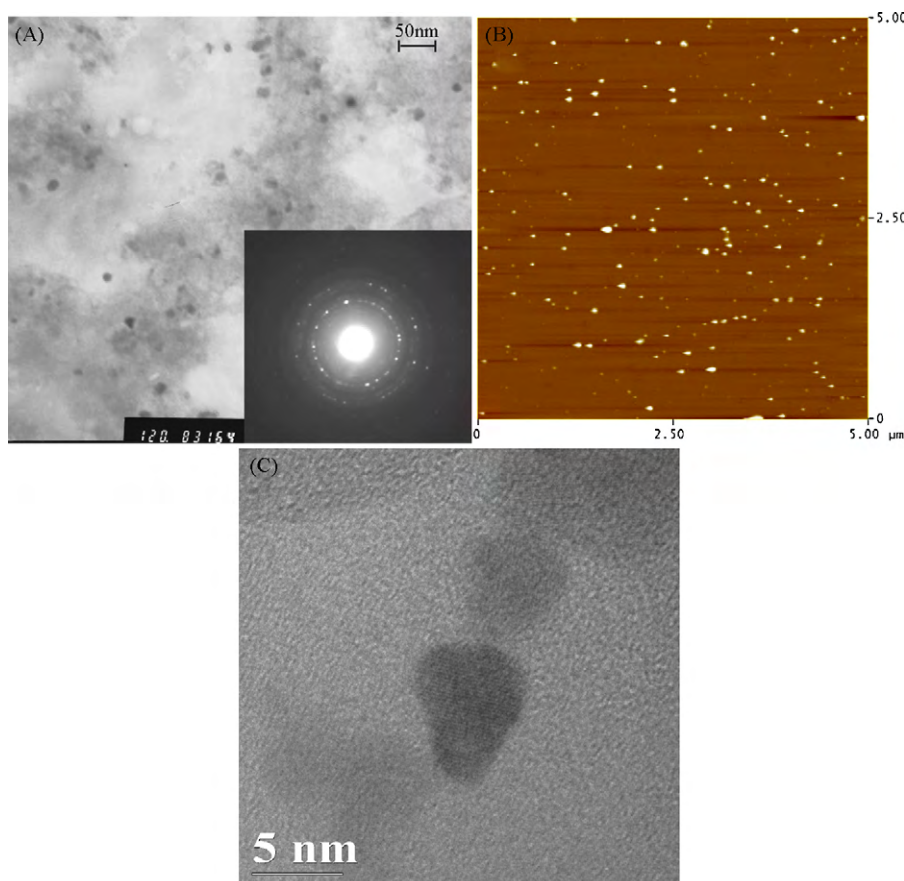


Fig. 1. TEM (A), AFM (B) and HRTEM (C) of  $CdWO_4$  solution collected at reaction time of 4 h.

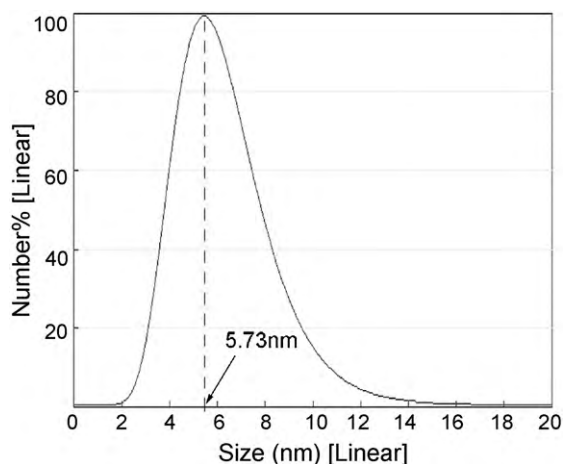


Fig. 2. PCS of CdWO<sub>4</sub> solution collected at reaction time of 4 h.

about  $8 \pm 2$  nm. SAED image with distinct electron diffraction lattices showed that the CdWO<sub>4</sub> QDs had a single-crystal structure. The irregular lattices of SAED resulted from several QDs with different phase taking part in electron diffraction. The particle size of monodisperse QDs was nearly normal distribution (PCS of QDs in Fig. 2). And lots of QDs' sizes were concentrated in 5.73 nm. There were no significant differences for particle size between TEM characterization and PCS measure.

### 3.2. IR analysis

IR pattern of CdWO<sub>4</sub> QDs collected after reaction time of 8 h was presented in Fig. 3. Due to -COOH of TGA converting to carboxylic salt through NaOH, there were two absorption bands which were nonsymmetrical vibration of  $1610\text{--}1550\text{ cm}^{-1}$  (-COO<sup>-</sup>) and symmetric vibration of  $1400\text{ cm}^{-1}$  (C-O). Characteristic absorption bands of R-CO-SR were located at  $1690\text{ cm}^{-1}$  [20]. Accordingly, both  $1395\text{ cm}^{-1}$  and  $1550\text{--}1710\text{ cm}^{-1}$  in Fig. 3 were corresponding to the book [20]. Absorption band of  $3020\text{--}3660\text{ cm}^{-1}$  was stretching vibration of  $\nu\text{-OH}$ . However, there were no absorption bands corresponding to  $950\text{--}1270\text{ cm}^{-1}$  based on reagents used in this experiment according to available literatures. This phenomenon might be attributable to IR displacement caused by size effect and peripheral functional groups of CdWO<sub>4</sub> QDs.

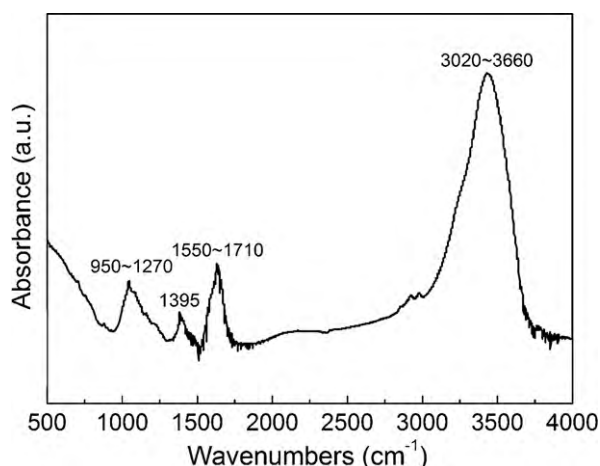


Fig. 3. IR pattern of CdWO<sub>4</sub> QDs collected at reaction time of 8 h.

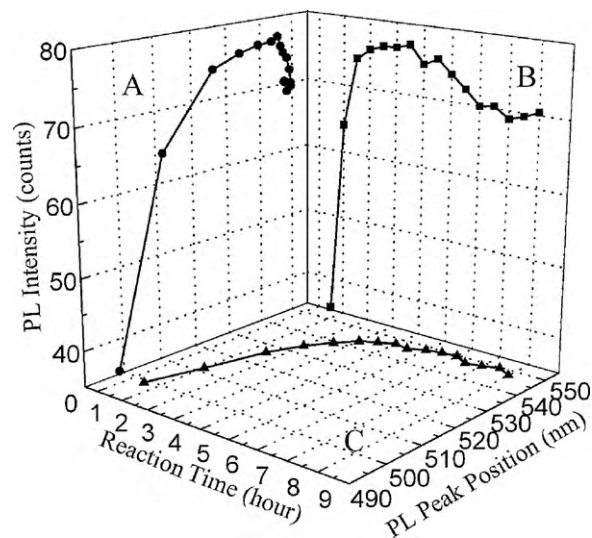


Fig. 4. PL's average value patterns of CdWO<sub>4</sub> QDs: (A) relationship between intensity and peak position; (B) relationship between intensity and reaction time; (C) relationship between reaction time and peak position.

### 3.3. Photoluminescence properties

In this experiment, the CdWO<sub>4</sub> QDs with wide excitation spectrum were excited at 330, 340, 350, 360, 370 and 380 nm, respectively. Therefore, the following data of Fig. 4 were average value for both PL intensity and peak position. The PL's data patterns of the as-prepared CdWO<sub>4</sub> QDs were presented in Fig. 4. With reaction time going, the position of PL peak was red-shift from 498 to 549 nm owing to particle size increasing (Fig. 4(C)), and intensity of PL increased first and then decreased (Fig. 4(B)). There were no sharply fluctuations of PL intensity and peak position as reaction time was beyond 4 h (Fig. 4(A and C)). According to the excitation spectra of the literature [21], there are two excitation bands which are near 290 nm and near 350 nm. Correspondingly, 490 and 570 nm luminescence bands of CdWO<sub>4</sub> crystals are excited in tungstate groups WO<sub>6</sub><sup>6-</sup> [21]. Because excitation wavelength selected in this work was near 350 nm which ranged from 330 to 380 nm, the luminescence bands of CdWO<sub>4</sub> QDs could be compared with the CdWO<sub>4</sub> crystal's luminescence bands of 570 nm (2.17 eV). The results showed that PL peak position of as-prepared CdWO<sub>4</sub> QDs was blue-shift compared with 570 nm WO<sub>6</sub><sup>6-</sup> luminescence center of bulk CdWO<sub>4</sub>, which was attributable to quantum size effect. PL peak position of traditional QDs formed by group II and group VI was red-shift with particle size increasing [22]. But, PL peak position of CdWO<sub>4</sub> QDs with WO<sub>6</sub><sup>6-</sup> luminescence center reached an upper limit of  $\sim 550$  nm in Fig. 3C. And PL property of CdWO<sub>4</sub> QDs was significantly different from that of traditional QDs.

### 3.4. Synthesis mechanism

Due to Cd atoms having 6-connecting nodes [23], -SH groups of six TGA linked with Cd ion via coordinate bond. When the tungstate groups were added and attacked the Cd ions at 100 °C, partial -SH groups linked with Cd ion could be replaced by tungstate groups. With reaction time going, many coordination compounds of tungstate groups linked with Cd ion combined each other to form the CdWO<sub>4</sub> embryos. Furthermore, "W/W" phase was formed by TGA. ["Water/Water" was abbreviated "W/W" in Fig. 5(B)]. And this "W/W" phase could be regarded as the "micro-reactor". "W/W" phase could be divided into two sections: one was inner water phase; another was external water phase. Owing to exclusion effect of QDs surface's carboxy groups with negative

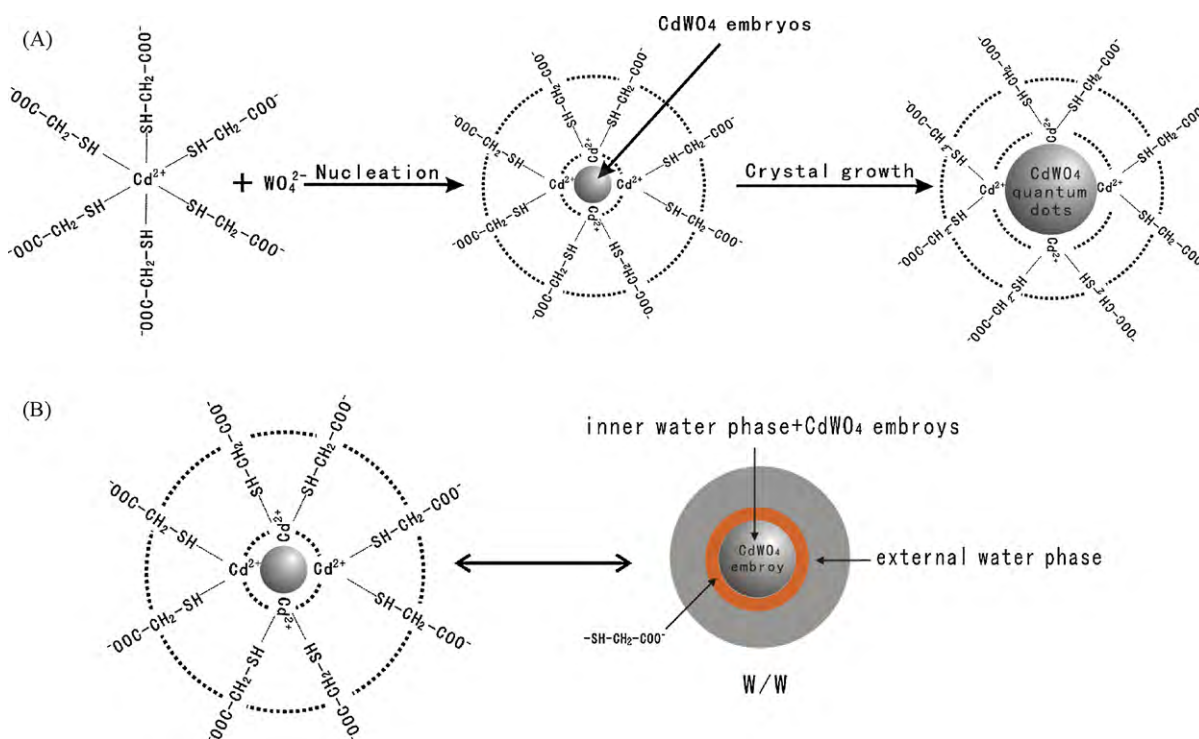


Fig. 5. The sketch map of the CdWO<sub>4</sub> QDs synthesis mechanism

charge, carboxy groups pointed at the external water phase. And CdWO<sub>4</sub> embryos were in the inner water phase. Gradually, the free tungstate groups entered into the “micro-reactor”. The Cd ions which linked with tungstate group and TGA also merged into the “W/W” phase. Then, CdWO<sub>4</sub> QDs came into being via crystal growth of CdWO<sub>4</sub> embryos. The sketch map of CdWO<sub>4</sub> QDs synthesis mechanism was presented in Fig. 5(A).

#### 4. Conclusion

- (1) Single crystal CdWO<sub>4</sub> QDs with a diameter of  $8 \pm 2$  nm was synthesized by aqueous phase modified-method. And the particles size of QDs was nearly normal distribution.
- (2) PL peak position of CdWO<sub>4</sub> QDs with WO<sub>6</sub><sup>6-</sup> luminescence center was blue-shift compared with 570 nm WO<sub>6</sub><sup>6-</sup> luminescence center of bulk CdWO<sub>4</sub>, and reached an upper limit of ~550 nm.
- (3) The synthesis mechanism of CdWO<sub>4</sub> QDs by “W/W” phase as “micro-reactor” was brought forward.

#### Acknowledgements

The authors are grateful to the financial support of the National Natural Science Foundation of China (No.: 10805069, 10875163).

#### References

- [1] T. Uematsu, H. Kitajima, T. Kohma, T. Torimoto, Y. Tachibana, S. Kuwabata, *Nanotechnology* 20 (2009) 215302.

- [2] M. Bruchez, M. Mario, G. Peter, W. Shimon, A.P. Alivisatos, *Science* 281 (1998) 2013.
- [3] W.C.W. Chan, S.M. Nie, *Science* 281 (1998) 2016.
- [4] K. Susumu, B.C. Mei, H. Mattoussi, *Nat. Protoc.* 4 (2009) 424.
- [5] J. Chen, C. Li, J.L. Song, X.W. Sun, W. Lei, W.Q. Deng, *Appl. Surf. Sci.* 255 (2009) 7508.
- [6] N. Sellami, A. Melliti, A. Sahli, M.A. Maaref, C. Testelin, R. Kuszelewicz, *Appl. Surf. Sci.* 256 (2009) 1409.
- [7] A.P. Alivisatos, *J. Phys. Chem.* 100 (1996) 13226.
- [8] R.E. Galian, M.D. Guardia, *Trac-Trend Anal. Chem.* 28 (2009) 279.
- [9] M. Nikl, E. Mihokova, M. Kobayashi, M. Ishii, Y. Usuki, V. Babin, A. Stolovich, S. Zazubovich, M. Bacci, P. Bohacek, *J. Lumin.* 87-9 (2000) 1136.
- [10] M. Nikl, P. Bohacek, E. Mihokova, N. Solovieva, A. Vedda, M. Martini, G.P. Pazzi, P. Fabeni, M. Kobayashi, M. Ishii, *J. Appl. Phys.* 91 (2002) 5041.
- [11] G.X. Zhang, R.P. Jia, Q.S. Wu, *Mater. Sci. Eng. B: Solid* 128 (2006) 254.
- [12] H.W. Liao, X.M. Liu, Y.D. Li, Y.T. Qian, Y.F. Wang, *Chem. Mater.* 12 (2000) 2819.
- [13] H. Lotem, Z. Burshtein, *Opt. Lett.* 12 (1987) 561.
- [14] K. Tanaka, S. Suzuki, C.K. Choo, *J. Appl. Phys.* 95 (2004) 1294.
- [15] K. Tanaka, T. Miyajima, N. Shirai, Q. Zhuang, R. Nakata, *J. Appl. Phys.* 77 (1995) 6581.
- [16] V.A. Pustovarov, A.L. Krymov, B.V. Shulgin, E.I. Zinin, *Rev. Sci. Instrum.* 63 (1992) 3521.
- [17] T.N. Nikolaenko, Y.A. Hizhnyi, S.G. Nediiko, *J. Lumin.* 128 (2008) 807.
- [18] Y.J. Yang, B.J. Xiang, *J. Cryst. Growth* 284 (2005) 453.
- [19] W.B. Xu, Y.X. Wang, R.H. Xu, S. Liang, G.X. Zhang, D.Z. Yin, *J. Mater. Sci.* 42 (2007) 6942.
- [20] K. Nakanshi, P.H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day Inc., 1977.
- [21] Y.A. Hizhnyi, S.G. Nediiko, T.N. Nikolaenko, *Nucl. Instrum. Methods A* 537 (2005) 36.
- [22] L. Melton, *Nature* 37 (2005) 775.
- [23] L. Han, W.N. Zhao, Y. Zhou, X. Li, J.G. Pan, *Cryst. Growth Des.* 8 (2008) 3504.