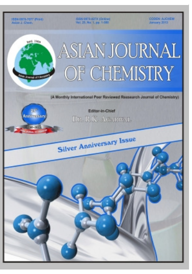
Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 3207-3210

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13594



Microwave-Assisted Solvothermal Synthesis and Characterization of $M_3V_2O_8$ (M = Ca, Cd) Nanoparticles

CHANG SUNG LIM

Department of Advanced Materials Science and Engineering, Hanseo University, Seosan 356-706, South Korea

Corresponding author: Tel/Fax: +82 41 6601445; E-mail: cslim@hanseo.ac.kr

(*Received*: 14 February 2012; *Accepted*: 14 December 2012) AJC-12549

$M_3V_2O_8$ (M = Ca, Cd) nanoparticles were synthesized successfully using a facile microwave solvothermal route followed by further heat-treatment. Well-crystallized $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles were formed after heat-treatment at 600 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 50-150 nm for $Ca_3V_2O_8$ and 50-200 nm for $Cd_3V_2O_8$. The synthesized $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and transmission electron microscopy. The optical properties were investigated by photoluminescence emission and Raman spectroscopy.

Key Words: $Ca_3V_2O_8$, $Cd_3V_2O_8$, Nanoparticles, Microwave-assisted solvothermal method, Lminescence, Raman spectroscopy.

INTRODUCTION

Metal orthovanadates have attracted considerable attention for potential applications in photoluminescence, IR-laser, light-emitting diode, photocatalyst, ferroelectric and microwave devices[1-3]. The metal orthovanadates have an orthorhombic crystal structure. Many inorganic or organic phosphors have already found for these white LED. Among various number of phosphors, metal orthovanadates have attracted considerable attention for potential applications in the broadband photoluminescence in the visible light range, as well as IR-laser, photocatalyst, ferroelectric and microwave devices. The broadband emission in the visible light range is effective to obtain a good colour rending property for the lighting devices.

Several processes have been developed over the past decade to enhance the applications of metal orthovanadates prepared by a range of processes, such as a solid-state reaction[4,5], a solution phase metathetic method[6], sol-gel[7], a solid-state metathesis approach[8], mechano-chemical method[9] and floating zone technique[10]. The chemical reactions between precursors powders have emerged as an attractive method to synthesize novel materials. Solid-state metathesis reactions require minimum energy input to initiate the synthesis reactions. There are several sources of providing the required energy such as contacting precursors with a heated filament, using electromagnetic waves. Microwave energy is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction with an electromagnetic field[11]. Hydrothermal process is an efficient low temperature method that allows the formation of particles with high degree of crystallinity and easy dispersion in an aqueous medium. The use of microwave energy in hydrothermal system promotes the development of a rapid heating to the required temperature with rapid rates of crystallization[12,13].

Recently, microwave solvothermal processes[14,15] have been reported the use of a facile and fast method in preparing nanocrystalline particles of metal tungstates with unique and enhanced properties. Solvothermal process is one of the most powerful methods employed for the crystallization of various unique nanoparticles. The solvothermal synthesis proceeds the reaction in a hot ethylene glycol solution as a polar solvent with a boiling point of 197 ºC. Microwave-assisted solvothermal reactions provide a facile route for the synthesis of $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles, which were obtained in the form of loosely connected nano-sized particles at considerably lower temperatures with a high pressure than those usually employed for their synthesis. When the microwave radiation is supplied to the ethylene glycol under a sealed pressure above boiling point, the components dissolving in the ethylene glycol are charged and vibrated in electric field interdependently. Therefore, it is possible to achieve rapid and uniform heating of microwave dielectric materials. Microwave solvothermal process using a solvent of ethylene glycol is a facile process that provides a high-qualified yield with cost-effective method in short time periods.

In present study, the $M_3V_2O_8$ (M = Ca, Cd) nanoparticles were synthesized using a facile solvothermal route assisted by the microwave irradiation. The characteristics of the synthesized

$M_3V_2O_8$ (M = Ca, Cd) nanoparticles are discussed based on the microwave solvothermal reaction in ethylene glycol under the high sealed pressure. The synthesized $M_3V_2O_8$ (M = Ca, Cd) nanoparticles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. The optical properties were examined by photoluminescence emission and Raman spectroscopy.

EXPERIMENTAL

Fig. 1 shows a flow chart for the synthesis of $M_3V_2O_8$ (M = Ca, Cd) nanoparticles by the microwave solvothermal process. $CaCl_2$, $CdCl_2\cdot 2H_2O$, Na_3VO_4 and ethylene glycol of analytic reagent grade (Aldrich) were used to prepare the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ compounds. Each of 0.012 mol $CaCl_2$ and 0.008 mol Na_3VO_4 for $Ca_3V_2O_8$ was dissolved in 30 mL ethylene glycol. In the same way, each of 0.012 mol $CdCl_2\cdot 2H_2O$ and 0.008 mol Na_3VO_4 for $Cd_3V_2O_8$ was dissolved in 30 mL ethylene glycol. The solutions were mixed and adjusted at a pH 9.5 using NaOH. The aqueous solution was stirred at room temperature. In the sequence, the mixture was transferred into a Teflon lined digestion vessel of 120 mL capacity. The aqueous solution was stirred at room temperature. In the sequence, the mixture was transferred into a Teflon-lined digestion vessel of 120 mL capacity. The Teflon vessel was placed into a microwave solvothermal autoclave (2.45 GHz, maximum power of 800 W). The microwave solvothermal conditions were kept at 200 ºC for 0.5 h. After microwave solvothermal process, the microwave autoclave was cooled at room temperature. The resulting solutions were treated with ultrasonic radiation and washed many times with distilled hot water. The white precipitates were corrected and dried at 100 ºC in a dry oven. The final products were heat-treated at 600 ºC for 3 h.

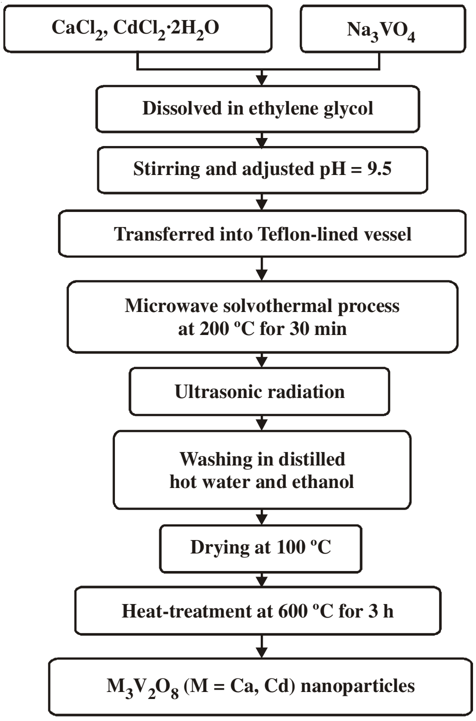


Fig. 1. Flow chart for the synthesis of $M_3V_2O_8$ (M = Ca, Cd) nanoparticles by the microwave solvothermal process

The existing phases of the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ particles after the microwave solvothermal process were identified by powder XRD (CuK_α, Rigaku D/MAX 2200, Japan). FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the absorption behaviour of the synthesized $Ca_3V_2O_8$ and $Cd_3V_2O_8$ particles over the frequency range, 400 to 4000 cm^{-1}. The microstructure, particle morphology and qualitative compositions of the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ particles were observed by TEM (JEM 2000-FX, 250 kV, Japan). The photoluminescence spectrum was recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Raman spectroscopy measurement was performed using LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as the excitation source, the power was kept at 0.5 mW on the samples.

RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the $Ca_3V_2O_8$ nanoparticles. All the observed diffraction peaks could be assigned to the trigonal phases, which is in good agreement with the crystallographic data of $Ca_3V_2O_8$ (JCPDS: 46-756, space group *R3c*)[8]. It suggests that microwave solvothermal synthesis is suitable for the growth of $Ca_3V_2O_8$ crystallites with the strongest major intensity peaks from the (210) and (220) planes planes with some preferred orientation, respectively.

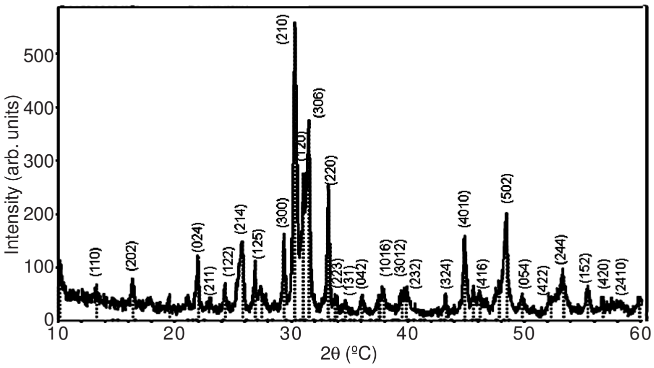


Fig. 2. XRD patterns of the $Ca_3V_2O_8$ nanoparticles synthesized by the microwave solvothermal process after heat-treatment at 600 ºC for 3 h

Fig. 3 (a, b) shows FT-IR spectrum of the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles in the wavenumber range, 4000-480 cm^{-1}. The large isolated absorbable peak around 820 cm^{-1} reveals typical characteristics of a strong V-O stretching in the $[VO_4]^{3-}$ in Fig. 3(a). The strong V-O stretching peaks are contributed to the uniform regular $[VO_4]^{3-}$ tetrahedron of the metal orthovanadates. The band at 1450 cm^{-1} is assumed that the samples prepared containing a small amount of surface-adsorbed water and alcohol in Fig. 3(a). The large isolated absorbable peak around 680 cm^{-1} in Fig. 3(b) reveals typical characteristics of a strong V-O stretching in the $[VO_4]^{3-}$. The strong V-O stretching peaks are contributed to the uniform regular $[VO_4]^{3-}$ tetrahedron of the metal orthovanadates.

Fig. 4 shows TEM images of the (a) $Ca_3V_2O_8$ and (b) $Cd_3V_2O_8$ nanoparticles. The TEM image of $Ca_3V_2O_8$ in Fig. 4(a) shows a well-defined and homogeneous morphology, showing the particle sizes of 50-150 nm. The TEM image of the $Cd_3V_2O_8$

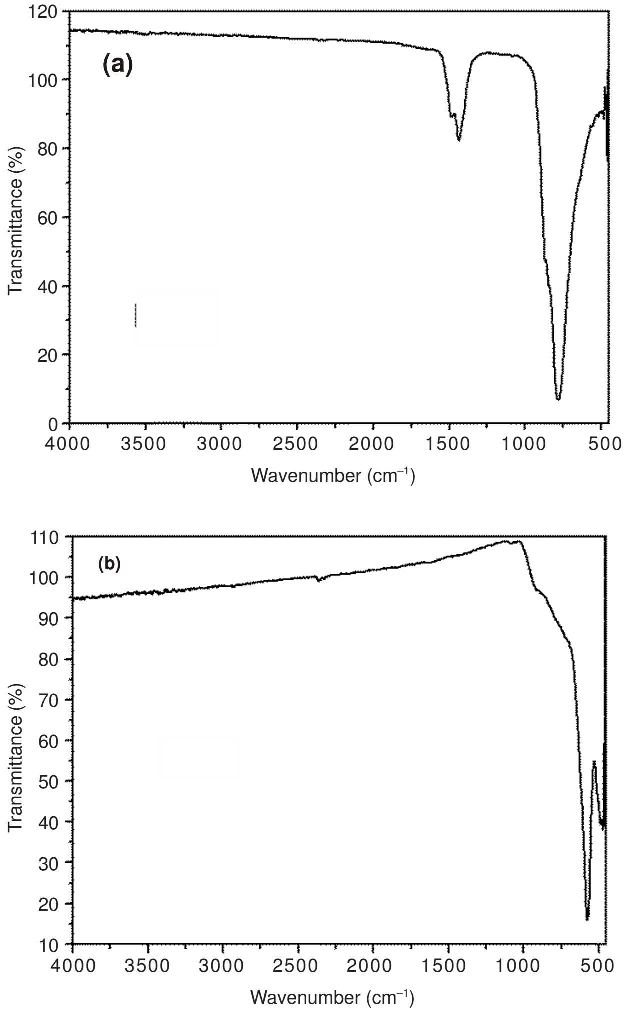


Fig. 3. FT-IR spectra of the (a) $Ca_3V_2O_8$ and (b) $Cd_3V_2O_8$ nanoparticles synthesized by the microwave solvothermal process after heat-treatment at 600 ºC for 3 h

in Fig. 4(b) shows a well-developed tetragonal morphology, showing the particle sizes of 50-200 nm. The microwave solvothermal process occurs in accordance with the reaction:

$$3MCl_2 + 2Na_3VO_4 \longrightarrow M_3V_2O_8 + 6NaCl$$

When the microwave radiation is supplied to the ethylene glycol under a sealed pressure above boiling point, the components dissolving in the ethylene glycol are charged and vibrated in electric field interdependently. The microwave solvothermal process is adjusted to heat the metal orthovanadates uniformly resulting in fine particles with a controlled morphology and to fabricate the product in a green manner without the generation of solvent waste. The microwave-assisted solvothermal reaction involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction in ethylene glycol accompanying the formation of NaCl with a high lattice energy. The microwave exothermic reaction occurs so rapidly that the temperature and the pressure of the ethylene glycol increases so quickly that the reaction products are essentially heated up. The microwave-assisted solvothermal reactions provide a facile and fast route for the synthesis of $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles at considerably lower temperatures with a high pressure than those usually employed for their synthesis. The well-defined $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles features synthesized by the microwave-assisted solvothermal process have a control over the morphology of the fine particles and can be used for technological applications.

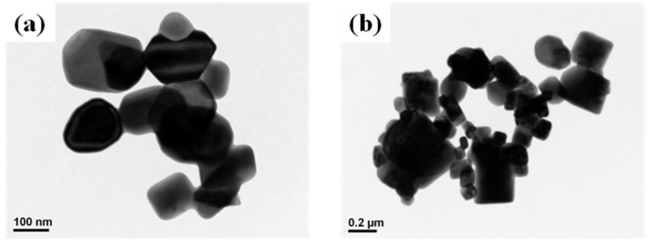


Fig. 4. TEM images of the (a) $Ca_3V_2O_8$ and (b) $Cd_3V_2O_8$ nanoparticles

Fig. 5 shows photoluminescence emission spectrum of the synthesized $Ca_3V_2O_8$ nanoparticles exited at 250 nm at room temperature. With excitation at 250 nm, $Ca_3V_2O_8$ particles exhibit major photoluminescence emissions in the blue wavelength range of 390-430 nm. The emissions of four narrow shoulders at approximately 490, 510, 530 and 530 nm are considered to form by defect structures. The emission spectra of metal orthovanadates are due mainly to charge-transfer transitions within the $[VO_4]^{3-}$ complex. The explanation of the narrow shoulders in Fig. 5 is proposed considering the Jahn-Teller splitting effect[16,17] on excited states of $[VO_4]^{3-}$ and anion in the $Ca_3V_2O_8$. This is similar to that reported by Zhan *et al.*[18]. The Jahn-Teller splitting effect essentially determines the emission shape of the $Ca_3V_2O_8$ particles. The additional emission bands can be interpreted by the existence of Frenkel defect structures (oxygen ion shifted to the inter-position with the simultaneous creation of vacancies) in the surface layers of the $Ca_3V_2O_8$ particles[19,20].

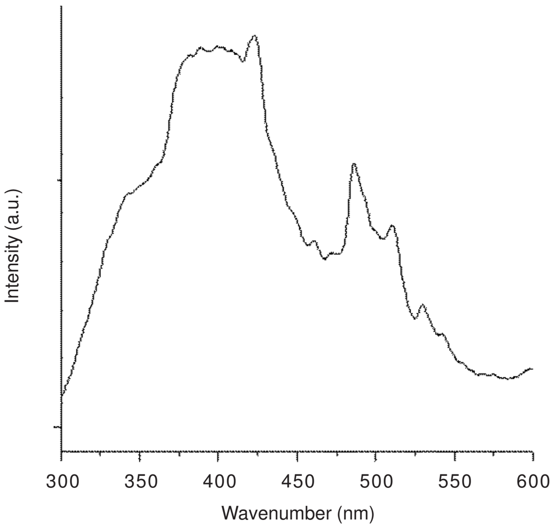


Fig. 5. Photoluminescence emission spectrumf the synthesized $Ca_3V_2O_8$ nanoparticles exited at 250 nm at room temperature

Fig. 6(a, b) shows Raman spectrum of the synthesized $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples. The vibration modes in the Raman spectra of the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles are classified into two groups, internal and external. The internal vibrations are related to the $[VO_4]^{3-}$

molecular group with a stationary mass center[21]. The Raman modes for the $Ca_3V_2O_8$ particles were detected at 858, 798, 409 and 357 cm^{-1}, the free rotation modes were detected at 282-234 cm^{-1} and the external mode was localized at 111 cm^{-1}. The Raman modes for the $Cd_3V_2O_8$ particles were detected at 675, 605 and 579 cm^{-1}, the free rotation modes were detected at 300-277 cm^{-1}. The well-resolved sharp peaks for the Raman modes for the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ particles indicate that the synthesized particles are highly crystallized.

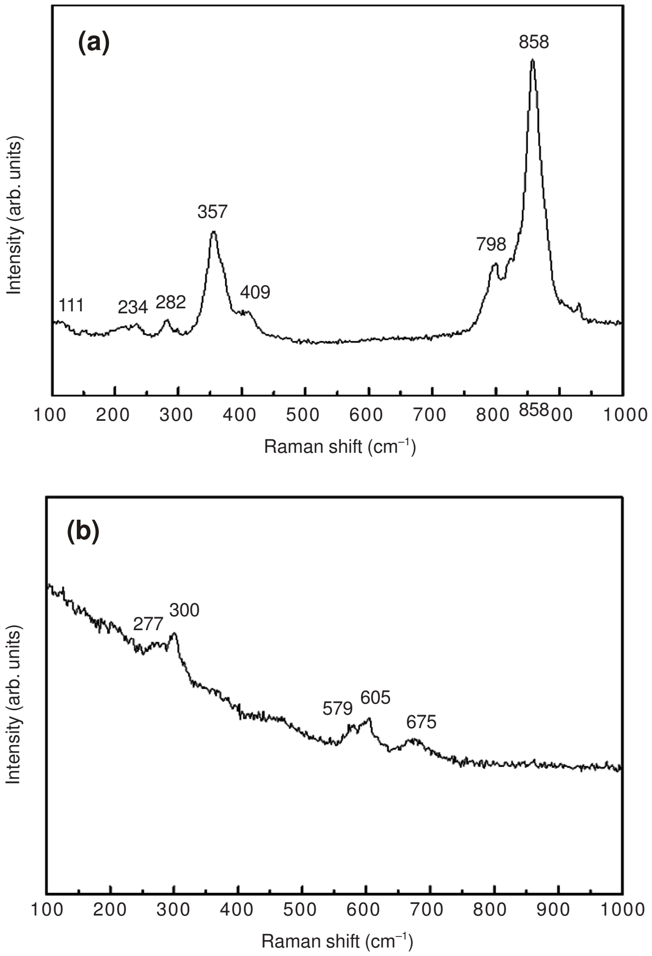


Fig. 6. Raman spectrum of the synthesized (a) $Ca_3V_2O_8$ and (b) $Cd_3V_2O_8$ nanoparticles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples

Conclusion

$Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles were synthesized successfully by the microwave solvothermal processes in a hot ethylene glycol solution as a polar solvent. The microwave solvothermal reactions occured so rapidly that the exothermic reaction was essentially used to heat up the metal orthovanadates. Well-crystallized $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles were formed after heat-treatment at 600 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 50-150 nm for $Ca_3V_2O_8$ and showing a well developed tetragonal morphology with particle sizes of 50-200 nm for $Cd_3V_2O_8$. With excitation at 250 nm, the $Ca_3V_2O_8$ nanoparticles exhibited major photoluminescence emissions in the blue wavelength range of 390-430 nm. The well-resolved Raman modes for the $Ca_3V_2O_8$ and $Cd_3V_2O_8$ nanoparticles indicated that the synthesized particles were highly crystallized.

ACKNOWLEDGEMENTS

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012-0007858).

REFERENCES

1. T. Nakajima, M. Isobe, T. Tsuchiya, Y. Ueda and T. Kumagai, *J. Luminescence*, **129**, 1598 (2009).
2. F. Yen, R.P. Chaudhury, E. Galstyan, B. Lorenz, Y.Q. Wang, Y.Y. Sun and C.W. Chu, *Physica B*, **403**, 1487 (2008).
3. N. Rogado, G. Lawes, D.A. Huse, A.P. Ramirez and R.J. Cava, *Solid State Commun.*, **124**, 229 (2002).
4. D. Wang, Z. Zou and J. Ye, *Res. Chem. Intermed.*, **31**, 433 (2005).
5. M. Kurzawa and A. Blonska-Tabero, *J. Therm. Anal. Calorim.*, **77**, 17 (2004).
6. P. Parhi and V. Manivannan, *Mat. Res. Bull.*, **43**, 2966 (2008).
7. S.S. Kim, H. Ikuta and M. Wakihara, *Solid State Ionics*, **139**, 57 (2001).
8. P. Parhi, V. Manivannan, S. Kohli and P. Mccurdy, *Bull. Mater. Sci.*, **31**, 885 (2008).
9. V. Manivannan, P. Parhi and J. Howard, *J. Cryst. Growth*, **310**, 2793 (2008).
10. R. Szymczak, M. Baran, J. Fink-Finowicki, B. Krzymanska, P. Aleshkevych, H. Szymczak, S.N. Barilo, G.L. Bychkov and S.V. Shiryaev, *J. Non-Crystalline Solids*, **354**, 4186 (2008).
11. S. Das, A.K. Mukhopadhyay, S. Datta and D. Basu, *Bull. Mater. Sci.*, **32**, 1 (2009).
12. K.P.F. Siqueira, R.L. Moreira, M. Valadares and A. Dias, *J. Mater. Sci.*, **45**, 6083 (2010).
13. J.C. Sczancoski, L.S. Cavalcante, M.R. Joya, J.A. Varela, P.S. Pizani and E. Longo, *Chem. Eng. J.*, **140**, 632 (2008).
14. J. Bi, L. Wu, Z. Li, Z. Ding, X. Wang and X. Fu, *J. Alloys Comp.*, **480**, 684 (2009).
15. T. Thongtem, A. Phuruangrant and S. Thongtom, *Curr. Appl. Phys.*, **8**, 189 (2008).
16. Y. Toyozawa and M. Inoue, *J. Phys. Soc. Jpn.*, **21**, 1663 (1966).
17. E.G. Reut, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **43**, 1186 (1979).
18. Y. Zhang, N.A.W. Holzwarth and R.T. Williams, *Phys. Rev. B*, **57**, 12738 (1998).
19. J. Van Tol and J.H. Van Der Waals, *Mol. Phys.*, **88**, 803 (1996).
20. V.B. Mikhailik, H. Kraus, D. Wahl and M.S. Mykhaylyk, *Phys. Status Solid B*, **242**, R17 (2005).
21. T.T. Basiev, A.A. Sobol, P.G. Zverev, L.I. Ivleva, V.V. Osiko and R.C. Powell, *Opt. Mater.*, **11**, 307 (1999).