



COMPUTATIONAL MODELING, ADVANCED SYNTHESIS AND APPLICATION OF ACID/BASE GASES AND SOME TOXIC FUMES TRAPPER FROM ATMOSPHERIC AIR

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ABSTRACT

Computational modeling of trapper was attempted by using computed program taking into our account the aim and the purpose of designated modeled structure. New promising nano-trapper was synthesized by applying solution route to obtain nano-product. The synthesized trapper characterized carefully by using X-ray diffraction to clarify the internal crystalline structure of investigated acid/base trapper. Scanning electron microscopy SEM and AFM were performed to evaluate both of particle and grain sizes of synthesized trapper. Furthermore many of spectral investigations were attempted. The synthesized nano-trapper classified into three categories first one is acid gas trapper with basic nature containing urea derivatives and second one is the basic gas trapper which is alumina containing trapper. The last trapper is designated to capture amphoteric gases and fumes. Acid/base gases under investigations like CO₂ and NH₃ were tested via synthesized nano-trapper. The efficiency of trapping process was monitored as a function on the particle size (exposure free surface area).

Key words: Modeling, Nano-synthesis, Trapper, Acid/base gases, SEM, XRD, AFM.

INTRODUCTION

Acid-gas-binding organic liquids/solids promise a more effective and less energy-intensive method to capture gases such as carbon dioxide and sulfur dioxide¹⁻⁵.

Initial work focused on CO₂ removal⁵⁻²⁰ but now variants target SO₂, ammonia,

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carbonyl sulfide and carbon disulfide. Each acid-gas-binding liquid consists of a mixture of an alcohol and a base. The liquid binds gas to form a colored ionic liquid. The system is selective because it chemically binds CO₂ as liquid alkylcarbonate salts, and the other gases as liquid alkyl-sulfite, alkylthiocarbonate and alkylthiocarbonate salts. Heating the liquid to a temperature between ambient and its boiling point (about 125°C) releases the gas and returns the liquid to its initial state.

Karror and Sirkar⁷ said the key challenges are to cut costs of the liquids. The researchers plan to look at new ways to make them-and how to deal with any water that gets into the system-work on easing phase separation of water will start by the end of 2009. The economic analysis will factor in the need for an initial water-removal step, he adds.

Researchers are also working on second-generation systems that use a single compound instead of a mixture. Post-combustion capture of CO₂ is one of the options considered for reduction of greenhouse gas emissions²¹⁻²⁷, since it can be integrated into existing power plants with relative ease. Solvent based technologies represent the leading capture technology being considered.

Their specific properties make amino-acid salts suitable for application in membrane gas absorption units, allowing compact equipment design and potentially leading to reductions in investment costs, Feron and Asbroek²⁶. Their oxygen resistance has attracted further attention to investigate flue gas applications as mentioned by Erga et al.²⁵ and Hook²⁷.

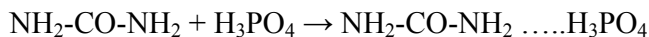
A further advantage can be achieved by the interesting feature of several amino-acid salts that solid precipitates are produced as the CO₂ loading exceeds a certain value. The precipitate consists of either the neutral amino-acid molecule, or a (bi) carbonate salt as reported by Kumar et al.¹²

These salts are obtained by neutralising the amino acid with potassium hydroxide. When a pure amino acid, with the overall formula HOOC-R-NH₂, is dissolved in water, the following equilibria are established: $\text{-H}^+ \text{-H} + \text{HOOC-R-NH}_3^+ \leftrightarrow \text{-OOC-R-NH}_3^+ \leftrightarrow \text{-OOC-R-NH}_2$ low pH neutral-mildly acid pH high pH. It is thus, seen that in solution the neutral molecule takes the form of a dipole, because the carboxylic group loses a proton while the amine group is protonated²⁸⁻³⁵.

The major goal of the present investigations are introducing new simple acid/base trapper with strong affinity towards both acidic and basic gases.

EXPERIMENTAL

Synthesis of carbamide phosphate acid/base gas trapper



Three equivalent weights of highly pure urea powder (16 g) was dissolved in 20 mL of ortho-phosphoric acid plus 20 mL of mixed methanol and acetone (1-3 ratio), respectively with supporting ultrasonic instrument. The crystallization process was performed using gently microwave assist to avoid any traces from applied solvent. The highly pure crystals from carbamide phosphate were dried in oven the forwarded for structural investigations.

Structural measurements

The X-ray diffraction (XRD): Measurements were carried out at room temperature on the fine ground samples using Cu-K α radiation source, Ni-filter and a computerized STOE diffractometer/Germany with two theta step scan technique. Rietveld and indexing of structure were made via Fullprof package and Gesas program.

Scanning electron microscopy (SEM): Measurements were carried out along ab-plane using a small pieces of the prepared samples by using a computerized SEM camera with elemental analyzer unit Shimadzu (Japan). Atomic force microscopy (AFM): High-resolution Atomic Force microscopy (AFM) is used for testing morphological features and topological map (Veeco-di Innova Model-2009-AFM-USA). The applied mode was tapping non-contacting mode. For accurate mapping of the surface topology AFM-raw data were forwarded to the Origin-Lab version 6-USA program to visualize more accurate three dimension surface of the sample under investigation. This process is new trend to get high resolution 3D-mapped surface for very small area.

Trapping efficiency measurements

The standard solutions of carbonic acid and ammonia both of concentration 0.2 M were applied as typical source of CO₂ and NH₃ gases, respectively. The solutions of 0.4 g carbamide phosphate (Trapper) were mixed with 25 mL of each (carbonic acid and ammonia) in different separated stoppered bottles for 1 hr with continuous shaking then filtered and the residual filtrate was titrated against 0.1 M of NaOH as standard solution using phenolphthalein as indicator in case of carbonic acid and 0.1 M HCl in case of ammonia.

RESULTS AND DISCUSSION

Phase identification

Figs. 1 a,b display the X-ray diffraction patterns of pure carbamide phosphate synthesized by simple solution route between pure urea and ortho-phosphoric acid as mentioned in the experimental part. The red pattern is for the experimental one while the blue pattern is for visualized carbamide phosphate. The ratio of fitting between both patterns are maximum referring to high figure of merits between experimental and theoretical patterns. These observations confirm that applied synthesizing solution route has good internal rearrangements of atomic coordinates inside crystal lattice structure.

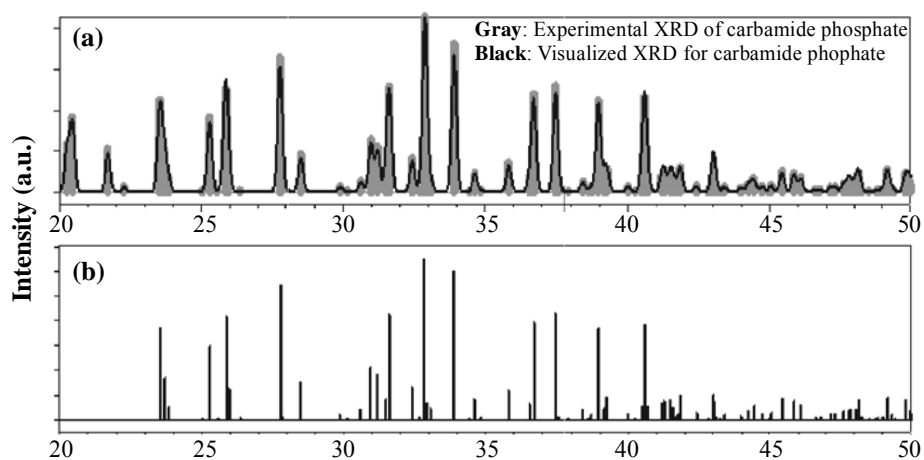


Fig. 1 a,b: Experimental and visualized XRD of nano-synthesized carbamide phosphate

Analysis of the corresponding 2θ values and the inter-planar spacing $d(\text{\AA})$ proved that, the compound mainly belongs to orthorhombic crystal structure with $Pbca$ space group as shown in Fig. 2 with evaluated lattice constant $a = 5.4321$, $b = 4.7.3011$ and $c = 8.3324 \text{\AA}$. The deficiency of oxygen atoms within the lattice may cause slight distortion on the orthorhombic crystal structure.

As shown in Fig. 2, the carbon atoms with yellow color and phosphorous atom with blue color are located in two different planes and the axial axis connected both planes are responsible for decreasing or increasing of c -axis lattice constant. The carbamide phosphate or urea phosphoric acid is simple compound linked together with hydrogen and coordinate bonding.

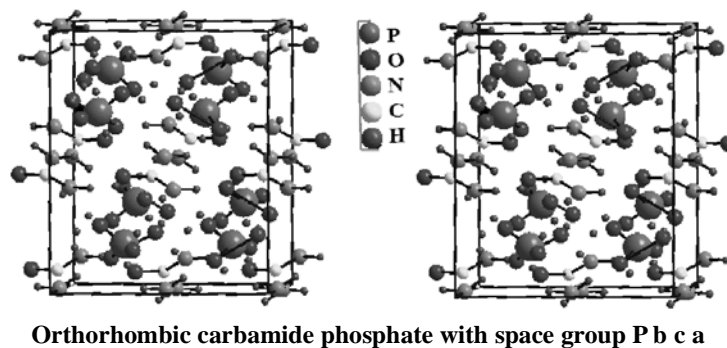


Fig. 2: Atomic arrangements of different atoms inside orthorhombic crystal structure

Table 1 indicates that the most intense reflection peak lies at ~ 33.04 with müller index [214] which is fully consistent with those mentioned in literatures³⁶⁻³⁸. Furthermore Table 2 show some selected bond distances, symmetry operations and torsion angles inside crystal lattice structure of nano-synthesized carbamide phosphate. It is clear that no violation was observed the phosphorous atom named P1 has three different bond distances P_1-O_1 , P_1-O_2 and P_1-O_3 , which are 1.099, 2.186 and 1.72 Å, respectively.

These variations in the bond length are due to environmental electronegative cloud are different inside the crystal lattice structure plus steric effect of bulky atoms as phosphorous.

Table 1: X-ray diffraction pattern data for measured carbamide phosphates

2 Theta	d-spacing	Intensity	F	h	k	l	Mult.
20.264	4.3787	387955.55	79.29	0	0	4	2
21.714	4.0895	344328.98	40.12	1	1	3	8
22.277	3.9874	39550.13	19.75	0	2	2	4
23.707	3.7500	339829.56	43.69	1	2	1	8
25.039	3.5534	3182.17	6.33	0	2	3	4
26.372	3.3768	7793.40	7.40	2	1	1	8
27.790	3.2077	1080448.12	92.10	1	2	3	8
28.485	3.1309	296162.00	70.01	0	2	4	4
30.119	2.9647	7240.74	8.22	2	1	3	8
31.619	2.8274	845857.25	93.56	2	2	1	8

Cont...

2 Theta	d-spacing	Intensity	F	h	k	l	Mult.
32.422	2.7592	266818.64	76.36	0	2	5	4
33.081	2.7057	893286.26	30.83	2	1	4	8
34.637	2.5877	157254.54	44.53	1	2	5	8
35.835	2.5038	231800.25	56.12	1	3	3	8
36.720	2.4455	783197.39	149.83	0	2	6	4
37.484	2.3974	850140.08	112.91	2	2	4	8
38.962	2.3098	39425.35	25.38	3	1	2	8
39.258	2.2930	179768.72	54.65	1	1	7	8
40.005	2.2519	42737.08	27.21	2	3	2	8

Table 2: Some selected bond distances and angles inside unit cell of carbamide phosphate

Atom 1	Atom 2	Sym. op. 2	d 1,2 Å	Atom 3	Symmetry op. 3	d 1,3 Å	Angle ^ 213
P1	O1	x, y, z	1.0901	O3	x, y, z	1.724	103.661
	O1	x, y, z	1.0901	H3	x, y, z	2.0595	78.366
	O1	x, y, z	1.0901	H5	x, y, z	2.1482	28.629
	O1	x, y, z	1.0901	O2	x, y, z	2.1862	121.494
	O1	x, y, z	1.0901	H5	-0.5+x, y, 0.5-z	2.2355	131.503
	O1	x, y, z	1.0901	H2	x, y, z	2.2884	37.713
	O1	x, y, z	1.0901	H4	x, y, z	2.4160	110.693
	O1	x, y, z	1.0901	N2	-0.5+x, y, 0.5-z	2.5591	127.431
	O1	x, y, z	1.0901	H2	0.5-x, -0.5+y, z	2.6669	135.044
	O1	x, y, z	1.0901	N2	x, y, z	2.7363	75.485
	O1	x, y, z	1.0901	H3	-0.5+x, y, 0.5-z	2.8492	126.967
	O1	x, y, z	1.0901	C1	-x, -0.5+y, 0.5-z	2.8689	165.598
	O1	x, y, z	1.0901	C1	x, y, z	2.9871	68.632
	O1	x, y, z	1.0901	O1	-0.5+x, y, 0.5-z	3.0557	121.607
	O1	x, y, z	1.0901	N1	x, y, z	3.0731	47.681
	O1	x, y, z	1.0901	N1	0.5-x, -0.5+y, z	3.1599	150.498
	O1	x, y, z	1.0901	N2	0.5-x, 0.5+y, z	3.2519	79.909

Nano-structural features of carbamide phosphate

Nano-structural features of carbamide phosphate were monitored by two different tools namely atomic force microscope (AFM) and scanning electron microscope (SEM) as clear in Figs. 3 and 4, respectively. Fig. 3 displays three dimensional image of the carbamide phosphate surface applying tapping mode technique. The analysis indicated that carbamide phosphate is crystalline materials packing in regular array structure with repeated specific heights as shown in Fig. 3 by orange line. The arrows and stars in Fig. 3 refer to heights gradient which appear at the surface with repeated multiple distances, these heights are due to steric bulky group outside lattice structure. The average grains size was estimated via AFM-grain-analyzer and found in between 12-230 nm, which confirm that solution route applied to synthesize carbamide phosphate yield to nano-product.

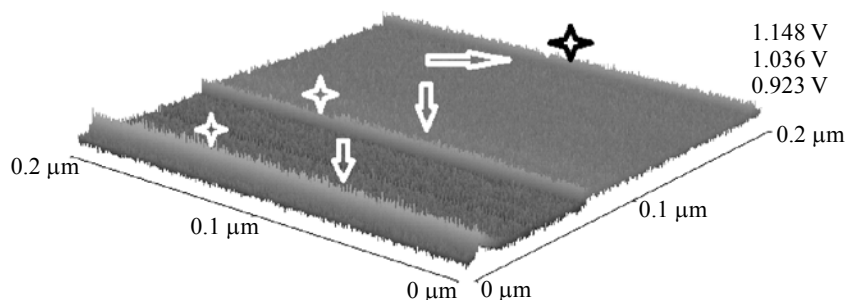


Fig. 3: 3D-AFM-micrograph-recorded for carbamide phosphate applying tapping mode

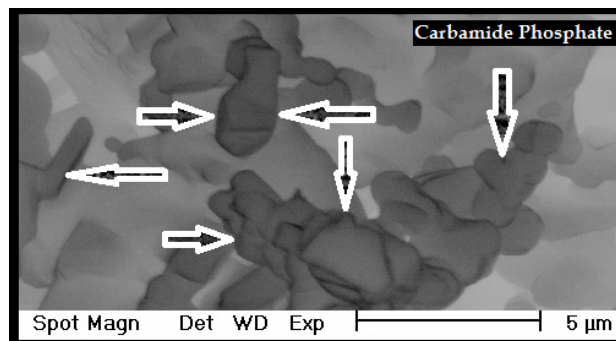


Fig. 4: SE-micrograph recorded for nano-synthesized carbamide phosphate

Fig. 4 shows SE-micrograph captured for carbamide phosphate for small piece. The average estimated grain size was found to be 220 nm, which is fitted with results obtained from AFM-microscopy.

Trapping efficiency measurements

The trapping efficiency was estimated as the amount mL mole gram molecular weight of gas existed determined by back titration. The standard solutions of carbonic acid and ammonia both of concentration 0.2 M were applied as typical source of CO₂ and NH₃ gases, respectively. The solutions of (0.4 g carbamide phosphate with grain size average 225 nm (Trapper) were mixed with 25 mL of each (carbonic acid and ammonia) in different separated stopper bottles for 1 hr with continuous shaking then filtered and the residual filtrate was titrated against 0.1 M of NaOH as standard solution using phenolphthalein as indicator in case of carbonic acid and 0.1 M HCl in case of ammonia. The results indicated that carbamide phosphate has very strong affinity towards CO₂ capture by ratio ~ 80% from first time while it records 66% capture for ammonia. These results confirmed that carbamide phosphate can play as dual trapper for both acidic and basic fumes gases.

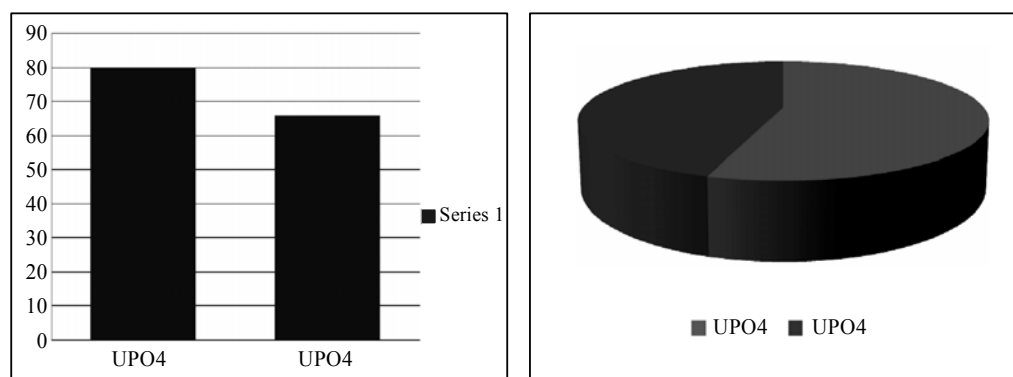


Fig. 5: Efficiency of trapping versus urea-phosphoric acid trapper (carbamide phosphate) (Efficiency CO₂ = 80% while NH₃ = 66%)

CONCLUSION

The conclusive remarks inside this article can be summarized in the following points -

- (i) Solution route is valid as technique of synthesizing nano-carbamide phosphate trapper.
- (ii) AFM & SEM investigations supported the average grain size ~ 225 nm.
- (iii) XRD analysis confirmed existence of orthorhombic crystal structure.
- (iv) Fitting between visualization and experimental confirmed our deductions.
- (v) Carbamide phosphate can act as dual trapper for acidic and basic gases.
- (vi) Carbamide phosphate is cheap and eco-friendly matter.

REFERENCES

1. J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg and K. Maskell (Eds.), *Climate Change: The Science of the Climate Change*, Cambridge University Press, London (1996).
2. H. Herzog, B. Eliasson and O. Kaarstad, *Capturing Greenhouse Gases*, *Sci. Am.*, **182(2)**, 72-79 (2000).
3. H. Herzog, *What Future for Carbon Capture and Sequestration ?* *ES & T*, **35(7)**, 148A-153A (2001).
4. A. Lyngfelt and B. Leckner, *Technologies for CO₂ separation*, in, *Min-isymposiumon Carbon Dioxide Capture and Storage*, School of Environmental Sciences, Chalmers University of Technology and Goteborg University, Goteborg, October 22 (1999).
5. A. Gabelman and S. T. Hwang, *Hollow Fiber Membrane Contactors*, *J. Membr. Sci.*, **159**, 61-106 (1999).
6. Z. Qi and E. L. Clussler, *J. Membr. Sci.*, **23**, 21-332 (1985).
7. S. Karoor and K. K. Sirkar, *Ind. Eng. Chem. Res.*, **32**, 674-684 (1993).
8. H. Kreulen, C. A. Smolders, G. F. Versteeg and W. P. M. Van Swaaij, *J. Membr. Sci.*, **78**, 217-238 (1993).
9. H. A. Rangwala, *J. Membr. Sci.*, **112**, 229-240 (1996).
10. Y. S. Kim and S. M. Yang, *Sep. Purif. Technol.*, **21**, 101-109 (2000).
11. Y. Lee, R. D. Noble, B. Y. Yeom, Y. I. Park and K. H. Lee, *J. Membr. Sci.*, **194**, 57-67 (2001).
12. P. S. Kumar, J. A. Hogendoorn, P. H. M. Feron and G. F. Versteeg, *Chem. Eng. Sci.*, **57**, 1639-1651 (2002).
13. P. H. M. Feron and A. E. Jansen, *Sep. Purif. Technol.*, **27**, 231-242 (2002).
14. H. Herzog and O. F. Pedersen, *The Kvaerner Membrane Aontactor: Lessons from a Case Study in how to Reduce Capture Costs*, in, *The Fifth International Conference on Greenhouse Gas Control Technologies*, Cairns, Australia, August 13-16 (2000).
15. H. Bosch, G. F. Versteeg and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, **45(5)**, 1167-1173 (1990).
16. S. Xu, Y. W. Wang, F. D. Otto and A. E. Mather, *Chem. Eng. Sci.*, **51(6)**, 841-850 (1996).

17. A. L. Kohl and F. C. Riesenfeld, Gas Purification, 4th Ed., Gulf Publishing, Houston, TX (1985).
18. G. Astarita, D. W. Savage and A. Bisio, Gas Treating with Chemical Solvents, Wiley, New York (1983).
19. D. Barth, C. Tondre and J. J. Delpuech, Chem. Eng. Sci., **39**, 1753-1757 (12) (1984).
20. W. C. Yu and G. Astarita, Chem. Eng. Sci., **40(8)**, 1585-1590 (1985).
21. H. Bosch, G. F. Versteeg and W. P. M. Van Swaaij, Chem. Eng. Sci., **44(11)**, 2723- 2734 (1989).
22. N. Haimour, A. Bidarian and O. C. Sandall, Chem. Eng. Sci., **42(6)**, 1393-1398 (1987).
23. G. F. Versteeg and W. P. M. Van Swaaij, J. Chem. Eng. Data., **33**, 29-34 (1988).
24. H. Kreulen, C. A. Smolders, G. F. Versteeg and W. P. M. Van Swaaij, Chem. Eng. Sci., **48**, 2093-2102 (1993).
25. O. Erga, O. Juliussen and H. Lidal, Carbon Dioxide Recovery by Means of Aqueous Amine, Energy Convers. Mgmt., **36(6-9)**, 387-392 (1995).
26. P. H. M. Feron and N. A. M. Asbroek, New Solvents Based on Amino- Salts for CO₂ Flue Gases Captures, Paper Presented at 7th International Conference on Greenhouse Control Technologies (GHGT-7), Vancouver, Canada (2004).
27. R. J. Hook, Ind. Chem. Eng. Res., **36**, 1779-1790 (1997).
28. IEA, The Characterisation of Carbon Dioxide and other Greenhouse Gas Releases from a Pulverised Coal Fired Combined Cycle Plat, IEA Greenhouse Gas R & D, Study Number IEA/91/OE9 (1992).
29. A. L. Kohl and R. B. Nielsen, Purification, Gulf Publishing Company, Houston, Texas (1997).
30. P. S. Kumar, J. A. Hogendoorn, P. H. M. Feron and G. F. Versteeg, Ind. Eng. Chem. Res., **42**, 12, 2832-2840 (2003).
31. G. F. Versteeg, P. S. Kumar, J. A. Hogendoorn and P. H. M. Feron, Method for Absorption of Gases, International Patent WO 03/095071 A1 (2003).
32. Commission of the European Communities, Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions, Limiting Global Climate Change to 2 Degree Celsius, The Way Ahead for 2020 and Beyond, Brussels, 10.1.2007. Com. (2007) 2 Final, EU: Brussels, Belgium.

33. The Intergovernmental Panel on Climate Change, IPCC Fourth Assessment Report, Working Group III, 20078, IPCC: Geneva, Switzerland (2007).
34. Carbon Sequestration Technology Roadmap and Program Plan, DOE/NETL (2006).
35. Ciferno, T. E. Fout, A. P. Jones and J. T. Murphy, Capturing Carbon from Existing Coal-Fired Power Plants, Chemical Engineering Progress, April (2009).
36. U. Ravi, K. Srinivasan, S. Anbukumar and P. Ramasamy, J. Cryst. Growth, **137**, 598–604 (1994).
37. Y. L. Geng, D. Xu, Y. L. Wang, W. Du, H. Y. Liu, G. H. Zhang, X. Q. Wang, D. L. Sun, J. Cryst. Growth, **273**, 624-628 (2005).
38. Y. L. Geng, D. Xu, D. L. Sun, H. Y. Liu and G. H. Zhang, X. Q., Mater. Chem. Phys., **90**, 53-56 (2005).

Revised : 03.11.2013

Accepted : 04.11.2013