

ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF BaB₆ FROM MOLTEN MELT

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Abstract

Barium hexaboride (BaB₆) crystals were electrochemically synthesized using molten salt technique. Barium carbonate (BaCO₃) and boron trioxide (B₂O₃) was used as reactants. Lithium fluoride (LiF) was used as the supporting electrolyte. The molten electrolyte consisted of 50 wt % BaCO₃ and B₂O₃ with different stoichiometric ratios of Ba and B and 50 wt % lithium fluoride. DTA/TGA studies were made to determine the eutectic point of the melt and it was found to be around 821°C. The electrolytic cell had a high purity graphite crucible, which served as the electrolyte holding vessel and also as the anode for the electrolysis. An electro-polished molybdenum rod was employed as the cathode. The electrolysis was performed at 870°C under argon atmosphere, at current densities ranging from 0.2-0.5 A/cm². The electrodeposited crystals were examined for the phase identification using X-ray diffraction technique. The AAS and the chemical analysis were made for the determination of chemical composition of the synthesized crystals. The purity of the crystals was also assessed using ICP-MS, XRF and EDX, which reveal that the crystals were associated with trace amount of impurities like oxygen, carbon and iron. The compound is found to be more than 99 % pure. The morphology of the crystals was examined using Scanning Electron Microscopy (SEM). From the above studies, it is concluded that the molten salt process is a simple preparative procedure for the synthesis of sub-micron size barium hexaboride crystals.

Keywords: Barium Hexaboride; Electrochemical Synthesis; DTA/TGA; XRD; AAS; SEM

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1. Introduction

Rare earth hexaborides have been the focus of extensive experimental and theoretical studies for over three decades [1]. Rare-earth and alkaline-earth metal borides belong to the group of non-oxide type metal-like compounds, characterized by a high melting point and high chemical stability. Other special properties, such as stable specific resistance, a low expansion coefficient at certain temperature ranges, diverse magnetic-orders, and high neutron absorbability [2,3] are also observed in this group of materials. They possess excellent corrosion and wear resistance, chemical inertness and thermal shock resistance than that of oxide ceramics. Many of these properties are of great interest for technical applications[4,5].

Borides can exist as a wide range of compositions and display structural features, which depend strongly on the metal and B ratio [6]. Structures with metal-rich composition, which are of sufficient size to accommodate the boron atoms as interstitial atoms. These structural features distinguish the boride structures from those of other refractory compounds.

The alkaline earth hexaborides were long thought to be simple polar semiconductors with single-particle gap energies of several tenths of an eV [7-9]. Recently great attention has been focused on divalent hexaborides after the discovery of ferromagnetism in La-doped CaB_6 [10] and their unusual magnetic properties [11-16]. The observation of ferromagnetism has been reported on the undoped systems of CaB_6 , SrB_6 , and La-doped BaB_6 [17-19]. This so-

called excitonic insulator is characterized by a condensation of bound electron-hole pairs (excitons). This controversial behavior in narrow gap semiconductors or semimetals was studied theoretically [20-21]. BaB_6 is a weakly ferromagnetic material with a Curie temperature TC well above the room temperature. From the results of D.C. magnetization measurements on single crystalline BaB_6 , the saturation magnetization at low temperatures is 8 times, in line with other weak ferromagnets of the hexaboride series [22].

Even though many studies have been attempted on their magnetic and electrical behavior, very few investigations [23,24] are reported on the synthesis of BaB_6 . Hence an attempt has been made to prepare pure BaB_6 crystals using simple chemicals by molten salt technique.

2. Experimental procedure

All the chemicals were of A.R. grade and obtained from Merck, India. The experimental arrangement for the synthesis of barium hexaboride is schematically shown in Fig. 1. The electrolytic cell had the provisions for adjusting the electrodes through a swagelok special arrangement. The cell consisted of a high-density graphite crucible supplied by M/S Graphite India Ltd. Bangalore, which served as the container for the electrolyte and also as the anode. The diameter of the graphite crucible was 7.5 cm and the depth was 10 cm. The cathode was made from a molybdenum rod of 1cm diameter fitted to a stainless steel rod. The graphite crucible was filled with the stoichiometric quantities of electrolyte salts

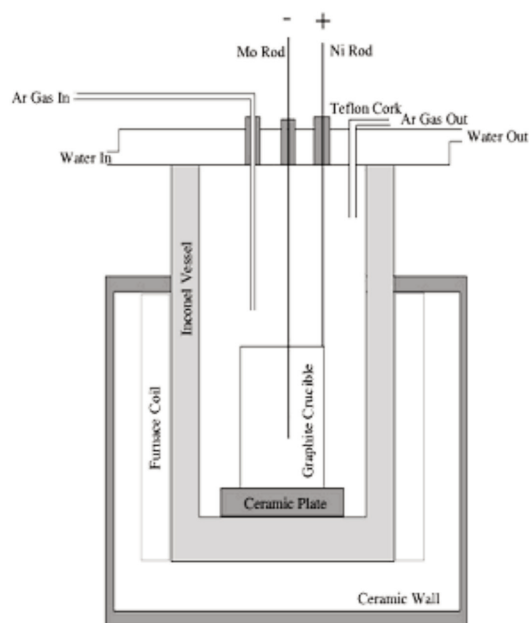


Fig 1. Schematic diagram of the experimental set up

consisting of BaCO_3 , B_2O_3 and LiF , which were dried at 450°C under argon atmosphere. The whole assembly was placed in an inconel reactor. The anode and the cathode were centrally positioned at the electrolytic cell.

Prior to the experiments, the eutectic point of the melt was determined by performing TG-DTA studies using Universal V4.3 instrument. Then, the salts were melted slowly under a continuous flow of argon gas. The melt was equilibrated at 875°C for one hour before proceeding electrolysis. An electro-polished molybdenum cathode was centrally positioned in the melt. The bath was pre-electrolyzed at ≈ 2.0 V for two hours to remove the impurities prior to electrolysis. Experiments were carried out at different current densities ranging from 0.2 - 0.5 A/cm^2

with the different molar ratios of Ba:B. After eight hours of electrolysis, the cathode was removed and the deposit was cooled in argon atmosphere. The deposit was then scraped off and the electrolyte adhering to it was leached with warm 5% HCl solution. Final washing was done with distilled water for several times. The weight of the deposit was determined and the nature of the powders were analyzed.

The phase identification of the powders was done using XRD - Philips XL30W/TMP X ray diffractometer. The morphology of the crystals was examined using a Scanning Electron Microscopy (SEM) Hitachi-S-3000H coupled with EDX. The chemical composition of the synthesized powders was analysed using PerkinElmer ICP-MS and Atomic Absorption Spectroscopy (AAS) and Horiba XGT2700 XRF Instruments.

3. Results and Discussion

The experiments were performed in LiF melt by the application of direct current as the energy source. On continuous flow of current in to the electrochemical cell, crystals of barium hexaboride was formed by the electro decomposition of BaCO_3 and B_2O_3 . After a period of 8 hours, a deposit of 1.2-1.5 cm thick was seen at the Mo cathode. The ultimate crystal size and the morphology are strongly depending upon the current density, temperature of the bath and duration of electrolysis. During electrolysis, the voltage across the cell was found to vary between 1.85 to 2.2 V.

The eutectic point was determined from differential thermal analysis (Fig. 2.) The

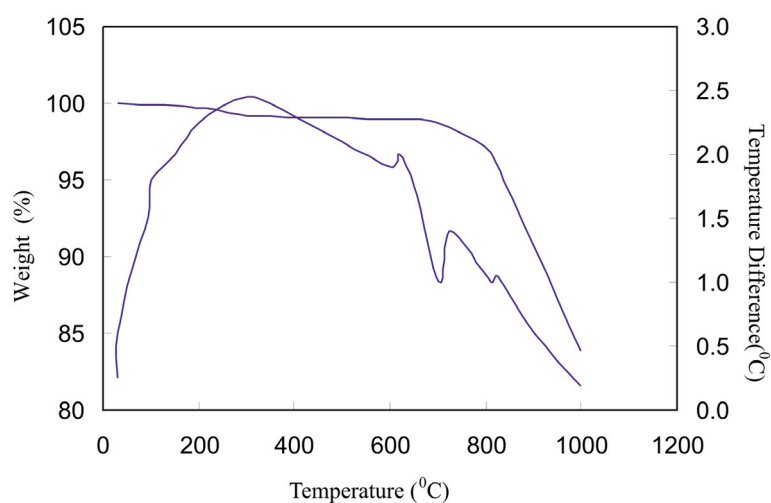


Fig 2. TG-DTA curves of the melts of LiF(50 wt %), BaCO₃ and B₂O₃ (50 wt %)

slight weight loss of the bath before the eutectic point may be due to the complete removal of moisture and decomposition of the BaCO₃. The eutectic point of the melt is found to be 821°C. The temperature of the electrolysis is kept approximately 50°C higher than the eutectic point to reduce the viscosity of the melt.

In all the experiments, it is observed that a good adherent deposit on the Mo cathode. At all the current densities, the color of the final product is found to be greenish-black.

The quantity of deposit is found to amplify with the increase in current density. The average crystalline size of the deposit is found to be inversely proportional to the current density.

The x-ray powder diffraction pattern of the synthesized BaB₆ crystals is shown in Fig. 3. The lattice constant value of BaB₆ is determined from the XRD data and it is found to be 4.27 Å at a current density of 0.5 A/cm². The XRD data exactly matches with the reported value [24]. The structure of

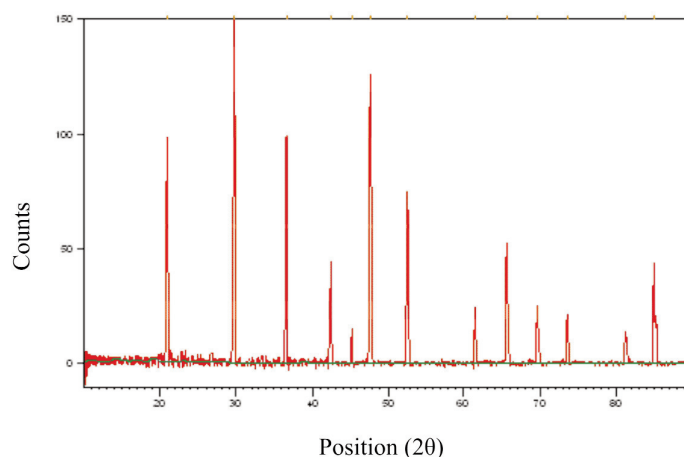


Fig 3. X-ray powder diffraction pattern of the product BaB₆

hexaborides, XB_6 , is simple cubic, with one large atom ($X = \text{Eu}, \text{Ca}, \text{Sr}$ or Ba) in the center and a B_6 octahedron in the corner [1]. It can be viewed as the CsCl-structure which is shown in Fig. 4. It is seen that the B_6^{2-} octahedron would be a pseudo-atom in the corner and the metal atom at the center is the second atom.

Atomic Absorption Spectroscopic (AAS)

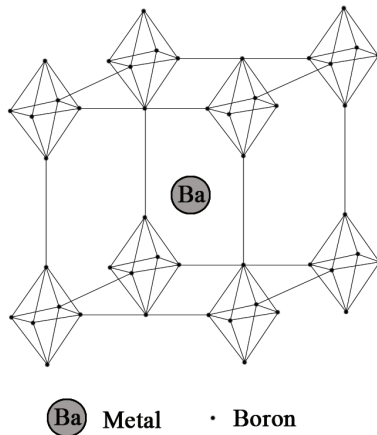


Fig 4. CsCl structure of BaB_6

analysis and the chemical analysis [25] show the stoichiometric ratios of Ba:B of BaB_6 . The ICP-MS, EDX and XRF studies ascertain the purity of the compound which is found to be more than 99% at all current densities. Traces of impurities such as carbon, oxygen and iron are identified. The impurity levels at a current density of 0.5 A/cm is given in Table 1.

Table 1: Impurities associated with BaB_6 crystals at the current density of 0.5 A/cm²

Impurity	Weight (%)
C	0.127
O	0.054
Fe	0.011

3.1 Mechanism of deposition of BaB_6

It is elucidated that both the components of the individual salts, which are dissolved in the ionic melt forming a thin layer of BaB_6 at electrode surface. The growth of the deposit is not limited by the solid-state diffusion and therefore boride layer with thickness up to 1.2-1.5 cm can be obtained in our experiments. The composition and morphology of the boride phase is being controlled by the process parameters, such as current density, cell voltage, temperature and composition of the bath.

The joint deposition of boron and barium in molten salts is explained by the so called ‘Unstable stoichiometric way’ [26-29] called ‘kinetic regime’ in the Russian literature [30]. This will appear if the deposition potentials of boron and the second component of the boride, i.e. the metal component (MC) on inert cathodes are too far from each other. Barium is found to be more electronegative than boron, so the depolarization of metal deposition should be taken into account. i.e. the condition is as follows:

$$\frac{\Delta G^{\circ} Me_x B_y}{nxF} \leq E_B^{inert} - E_{Me}^{inert}$$

Where, n^- is the valence of metal ions, Me^{+n} dissolved in the melt and participating in the synthesis of the boride phase $Me_x B_y$. When the above condition is fulfilled, first the macroscopic layer of one of the components will be deposited on the cathode and the formation of boride will take place during depositing the second component on this layer with depolarization. In this case the

synthesis of boride is possible only above the limiting current density of the more electropositive component. Hence, the composition of the boride phase will strongly depend on the concentration of the ions of the more electropositive component in the melt i.e., boron concentration. It also depends on the actual cathodic current density. It has been reported that during the crystal deposition, both the composition of the melt and the effective cathode surface area will continuously change, hence, the final composition of the boride will also be changed. This mechanism has been reported as 'unstable stoichiometry way' [26-29]. It is emphasized that coatings with relatively stable stoichiometry can also be obtained, if one should keep the composition of the melt constant and to keep the growing boride phase ideally planar during the process. This would ensure a constant ratio of partial current densities of the two components of the boride during the deposition process. Boron and metal atoms both are deposited at more positive potentials than their own equilibrium deposition potentials usually get dissolved in the melt again. But, if such unstable boron and metal atoms appear to be in contact, they will stabilize each other with the formation of the stable boride phase [31].

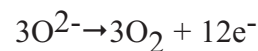
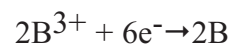
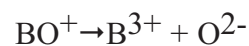
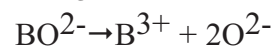
The reaction temperature plays an important role in determining the shape of the final product [32]. The explanation is based on the following factors that the final shape of the particles is decided by two different crystalline phases, [100] and [111], where the [111] phase has a higher surface energy than the [100] phase. Therefore, at higher temperatures the [111] phase has gained more thermal energy, which leads to

the formation of the most stable phase of the cubic morphology.

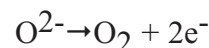
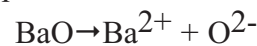
Galina et al.[33] define the kinetic characteristic of boron electro-reduction in chloride-fluoride melts and it is identified as the one step process, controlled by the charge transfer reaction.

LiF increases the fluidity and the electrical conductivity of the melt. It is more stable at high temperatures and its decomposition potential is found to be more cathodic than any other salts chosen. The presence of LiF in the electrolyte has a definite role on the deposition of this compound [34,35]. The electro-deposition process has also influenced by the pre-electrolysis and virginity of the cathode surface. It is noted that the average grain size of the deposit decreases with increasing current density, decreasing temperature and the concentration of the electrochemically active species.

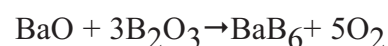
According to Uchida et al.[36] the electro decomposition of boron from B_2O_3 can be written as follows.



The decomposition of BaO may be represented as follows,



The overall cell reaction can be written as:



As per the above reaction, barium and boron are reduced at the Mo cathode to form BaB₆. The oxygen is evolved at the anode.

The mechanism of crystal formation of hexaboride may be similar as solid state reaction at high temperature, explained by Gedanken et al. [37]. According to him preliminarily, the particles of B and Ba are agglomerated, without any particular shape and are in the bath. The deposited boron on the molybdenum cathode acts as the nucleation center for the formation of hexaboride. It converts into small primary crystalline particle at high temperature. It is elucidated that the formation of the cubic morphology by thermodynamically controlled process. Finally, the fine crystalline particles are joined together to form submicron sized crystals. Ultimately, the perfect cubic structure is obtained by

electro-deposition at the cathode surface at 900°C, due to Ostwald ripening process [38].

The SEM images show that the cubic nature of the BaB₆ crystal at all current densities. The SEM micrographs recorded for the sample obtained at 0.3 A/cm² is shown in Fig.5. The cathodic current density is found to influence the morphology of boride crystals. While at higher densities, it is observed that the deposit is in dendritic nature.

It has been inferred that the electro-chemical synthesis of BaB₆ has found to possess the following advantages.

- i) Smooth coatings to loose dendrite crystals can be deposited by varying the current density and other process parameters.
- ii) It is a low temperature synthesis route with cheap and simple technological input from the economic point of view.

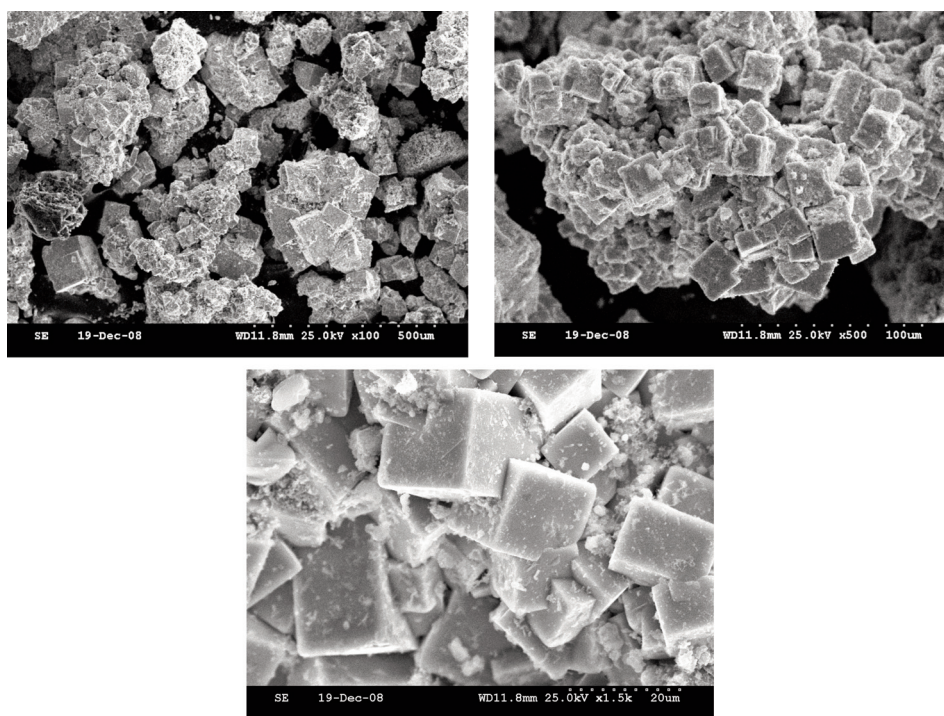


Fig 5. SEM Micrographs of BaB₆

4. Conclusions

The molten salt process demonstrates that it is a simple preparative technique for the synthesis of sub-micron size barium hexaboride crystals. Current density plays an important role on the morphology of the crystals. This electro synthesis process is found to be an economically viable process for the large scale preparation.

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References

1. V. I. Matkovich, Boron and Refractory Borides, Springer-Verlag, Berlin, 1977.
2. K. Segawa, A. Tomita, K. Iwashita, M. Kasaya, T. Suzuki, S. Kunii, J. Magn. Magn. Mat., 104 (1992) 1233.
3. C. L. Perkins, M. Trenary, T. Tanaka, S. Otani, Surf. Sci., 423 (1999) L222.
4. C.M. Chen, W.C. Zhou, L.T. Zhang, J. Amer. Ceram. Soc., 81 (1998) 237.
5. Shu-Qi Zheng, Zeng-Da Zou, Guang-Hui Min, Hua-Shun Yu, Jian-De Han, Wei-Ti Wang, J. Mat. Sci. Lett., 21 (2002) 313.
6. T. Lundström, Pure and Appl. Chem., 57(10) (1985) 1383.
7. J. Etourneau, J.P. Mercurio, P. Hagenmueller, Boron and Refractory Borides, edited by V.I. Matkovich (Springer), 1977, p. 115.
8. R.W Johnson. and Daane A.H., J. Chem. Phys., 38 (1963) 425.
9. J. Etourneau, J.P. Mercurio, R. Naslain, P. Hagenmueller, J. Solid State Chem., 2 (1970) 332.
10. S.E. Lofland, B. Seaman, K.V. Ramanujachary, N. Hur and S. W. Cheong, Phys. Rev. B 67 (2003) 020410.
11. D. Ceperley, Nature, (London) 397(1999) 386.
12. G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett., 82 (1999) 5317.
13. M. E. Zhitomirsky, T.M. Rice and V. I. Anisimov, Nature, (London), 402 (1999) 251.
14. L. Balents, C.M. Varma, Phys. Rev. Lett., 84 (2000) 1264.
15. V. Barzykin, L. P. Gor'kov, Phys. Rev. Lett., 84 (2000) 2207.
16. J. D. Denlinger, J. A. Clack, J.W. Allen, G.H. Gweon, D.M. Poirier, C.G. Olson, J. L. Sarrao, A.D. Bianchi and Z. Fisk, Phys. Rev. Lett., 89 (2002) 157601.
17. P. Vonlanthen, E. Felder, L. Degiorgi, H. R. Ott, D. P. Young, A. D. Bianchi, Z. Fisk, Phys. Rev., B, 62 (2002) 10076.
18. J.L. Gavilano, B. Ambrosini, H.R. Ott, D.P. Young, Z. Fisk, Physica B, , 281-282 (2000) 428.
19. T. Terashima, C. Terakura, Y. Umeda, N. Kimura, H. Aoki and S.Kunii, J. Phys. Soc. Jpn., 69 (2000) 2423.
20. J.D. Cloizeaux, J. Phy. Chem. Solids, 26 (1965) 259.

21. B. I. Halperin, T. M. Rice, *The Excitonic State at the Semiconductor-Semimetal Transition in Solid State Physics*, Edited by Seitz F., Turnbull D and Ehrenreich H. (Academic Press, N.Y.), 1968, p.115.
22. Sh. Mushkolaj, J.L. Gavilano, D. Rau, H. R. Ott, A. Bianchi, Z. Fisk, *Acta Physica Polonica B*, 34(2) (2003) 1537.
23. T. I. Serebryakova, E.V. Marek, *Powder Metallurgy and Metal Ceramics*, 8(8) (1969) 4.
24. G. Min, S. Zheng, Z. Zou, H. Yu, J.Han, *Materials Letters*, 2003, 57 (7)1330.
25. H. Blumenthal, *Anal. Chem.*, 23 (7) (1951), 992.
26. S.V. Devyatkin, G. Kaptay, J.C. Poignet, J. Bouteillon, *Molten Salts Forum*, 5-6, (1998), 331.
27. F.X. McCawley, C. Wyche, D. Schlain, *Pat. USA3697390*.
28. F.X. McCawley, C. Wyche, D. Schlain, *Pat. USA3827954*.
29. V.I. Shapoval, C. Kaptay, S.V. Deviatkin, N. Masuko, T. Osaka, Y. Ito, *Electrochemical Technology: Innovation and New Developments*, co-published by Kodansha Ltd and Gordon and Breach Science Publishers, S.A. 1996, p. 361.
30. C. Kaptay, E. Buzinkay, *Molten Salts Forum*, 5-6 (1998) 359.
31. G. Kaptay, S.A. Uznetsov, *Plasmas & Ions*, 2 (1999) 45.
32. S.M. Lee, S.N. Cho, J. Cheon, *Adv. Mater.*, 15 (2003) 441.
33. A. Galina, G.A. Bukatova, S. A. Kuznetsov, *Electrochem. Comm.*, 7 (2005) 637.
34. E. Stefanidaki, C. Hasiotis, C. Kontoyannis, *Electrochimica acta*, 46 (2001) 2665.
35. P. Chamelot, L. Massot, C. Hamel, C. Nourry, P. Taxil, *J. Nuclear Materials*, 360 (2007) 64.
36. K. Uchida, *Surface Tech.*, 7 (1978) 137.
37. R. Kalai Selvan, I. Genish, I. Perelshtein, M.J. Calderon Moreno, A. Gedanken, *J. Phys. Chem. C*, 112 (6) (2008) 1795.
38. J. Zeng, H. Wang, Y. Zhang, M.K. Zhu, H. Yan, *J. Phys. Chem. C*, 111 (2007) 11879.