NANOSTRUCTURED METAL BORIDES: SYNTHESIS AND PROPERTIES

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by

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Department of Chemistry

Submitted in accordance with the requirement for the Degree of Doctor of Philosophy

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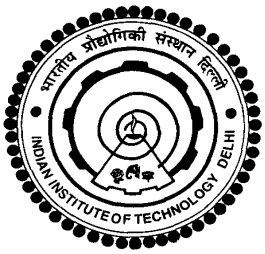

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

JUNE, 2012

To my husband

and

all family members

CERTIFICATE

This is to certify that the thesis entitled, **"Nanostructured Metal Borides: Synthesis and properties"**, being submitted by **Mrs. Menaka**, to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Mrs. Menaka has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

Date**:**

Place: New Delhi

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Professor

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Menaka

Abstract

Metal borides are considered as important technological materials because of its properties such as high melting point, hardness, wear/corrosion/oxidation resistance, excellent thermal and electrical properties. Based on the stoichiometry (boron to metal ratio), metal borides are broadly classified into two categories (1) metal rich borides (where boron to metal ratio is less than 4) and (2) boron rich borides (where boron to metal ratio is more than equal to 4). Metal-rich borides are mainly composed of transition metal and boron while boron-rich borides are formed by combination of metal (like main group element, lanthanides and actinides) with boron. These borides have tremendous technological application in photonics and electronics devices. Metal diboride like magnesium diboride, a superconductor (Tc = 39 K) is used in modern MRI applications while metal hexaboride like lanthanum hexaboride is widely used in making electron guns (source of electrons) in electron microscopes. Apart from the commercial applications, metal borides have interesting chemistry due to its complex chemical structure formed by the varying arrangement of boron atoms to yield chains and network structures. Most of the boron-rich borides generally show high hardness, thermal and electrical conductivity. Apart from immense scientific and industrial applications, the major issue in metal borides is its difficult synthetic conditions (high pressure and high temperature). Hence, there have been very few studies so far on **nanostructured** metal borides. Metal borides are generally synthesized using solid state route which tends to occur at high temperature (1500°C-2500°C) and results in large particles. Metal diboride thin films have been obtained via chemical and physical vapour deposition techniques which require gaseous reagents and expensive equipment. There are a few studies via

high temperature solvothermal route, however, the control of shape and size is not possible and generally yield micron-sized particles. *The present thesis is aimed to develop economical routes to synthesize nanostructured metal borides which have industrial and strategic applications.* Among many metal borides, we have focused on the synthesis of metal diborides (CrB_2, NbB_2 and ZrB_2) and metal hexaborides (LaB_6, CeB_6 and $La_{1-x}Ce_xB_6$). Metal diborides MB_2 (M= Ti, Zr, Hf, Nb and Ta) are highly refractive with high hardness and strength and also act as excellent electrical conductors. Moreover, some metal diborides show oxidation resistance (chromium diboride) and remarkable magnetic and catalytic properties. Among the rare earth hexaborides, LaB_6 with a melting point of $2500^{O}C$, high electrical conductivity, low work function (~2.6 eV) and low vapour pressure at high temperature makes it one of the best thermionic material for high electron density cathode. The control of size and morphology of metal borides in the nanoregime have been achieved by the borothermal reaction of metal precursor at low temperature. In this study, we have developed the processes to obtain various metal precursors using reverse micellar and hydrothermal route and then employed borothermal reduction of these precursors in inert atmosphere leading to the formation of nanostructured metal borides. We have carried out detailed structural and microscopic studies and also evaluated the magnetic, anticorrosion and field emission properties of these metal borides in the nanometer regime.

In chapter 1, a detailed survey of the background literature has been carried out for the state of knowledge existing in the area relevant to the metal with interesting mechanical and field emission properties. We also discuss the possibility for obtaining metal borides in bulk as well as nano regime. Though the various high temperature routes

are known which, cannot be commercialized due to difficult synthetic condition. In the the introduction section, we have also discussed the details of our effort for designing of the new methods to obtain nanostructured metal borides (especially metal diborides and metal hexaboride) of controlled size, morphology and properties.

In chapter 2, we have discussed the method of synthesis of nanostructured lanthanum hexaboride of various shape and sizes and their size dependent field emission properties. In this chapter, we aimed to develop a low temperature route to synthesize lanthanum hexaboride with controlled shape and sizes. For the preparation of lanthanum hexaboride, lanthanum hydroxide precursor was prepared by the reverse micellar (microemulsion) route. In the reverse micellar route we have varied the surfactant during the synthesis of lanthanum hydroxide precursor and we found that the non-ionic surfactants led to the growth of nanoparticles (10 nm) of lanthanum hydroxide precursor while the cationic surfactant led to the formation of flower like structure (made up of spindles, dia = 0.25 μm, length= 2.25 μm). We have also investigated the effect of non polar phase on the morphology of the lanthanum hydroxide precursor using CTAB/non-polar/1-Butanol/ aq. system (A= isooctane, cyclohexane and hexane). As discussed earlier, the cyclohexane as a non polar phase leads to the formation of flower like structure while iso-octane and hexane lead to the formation of rods (dia:100 nm and length 1 μm) and spheres (0.2 μm) respectively. Further reaction of lanthanum hydroxide precursor with boron (purified boron homogeneously mixed with lanthanum hydroxide precursor by grinding) in inert atmosphere at 1300°C led to the formation of pure cubic lanthanum hexaboride (a = 4.15 Å) as confirmed from powder x-ray diffraction studies.

Transmission electron micrographs of lanthanum hexaborides obtained by different lanthanum precursors shows the formation of the various morphologies (spheres and rods). We have also fabricated the lanthanum hexaboride film using spin coating route.

Further the atomic force microscopic studies of the lanthanum hexaboride films obtained from dispersed nanorods (dia 20 nm and length 120 nm) shows a vertical orientation of the nanorods over the silicon substrate (Figure 4) without using any template. This methodology does not require any template for obtaining these vertically aligned nanorods. The field emission properties can be tuned by controlling the shape and size of the lanthanum hexaboride nanostructures.

In Chapter 3, the synthesis and field emission properties of cerium hexaboride nanorods have been carried out. Cerium hexaboride is well –known for filaments of electron microscope due to its field emission properties (high brightness electron source) and has a long service life. The synthesis of cerium hexaboride (and most other borides) normally requires very high temperatures (1500°C–1700°C) and high pressure. Thus, low temperature synthesis of cerium hexaboride at ambient pressure is a challenge. In chapter 3, we try to obtain vertically aligned cerium hexaboride nanorods which offers better field emission properties with highest field enhancement factor reported so far. The optimization of the process to obtained vertically aligned cerium hexaboride nanorods involves in three different stages. First, the low temperature synthesis of polycrystalline cerium hexaboride, second, the fabrication of cerium hexaboride films (by spin coating and slow evaporation) having vertically oriented nanorods and third the enhancement in field emission properties. The synthesis of cerium hexaboride nanorods has been carried out by low temperature borothermal reduction process using a cerium precursor

(synthesized via reverse micellar route and hydrothermal route) and boron as starting materials. The borothermal reduction of cerium precursors have been carried out at low temperature (~ 1300°C) and ambient pressure in inert atmosphere. The field emission studies of the vertically aligned nanorods of diameter 30 nm and diameter 200 nm show a field enhancement factor of 3863 and 3658 respectively which is nearly seven-fold higher than the maximum field enhancement factor known so far.

In chapter 4, we have shown the methodology for the development of a simple approach to stabilize polycrystalline lanthanum cerium hexaborides without using any flux and at ambient pressure. The nanostructured lanthanum-cerium borides were synthesized using hydroxide precursors. These precursors ($La_{1-x}Ce_x(OH)_3$, x=0.1,0.2,0.3 and 0.5) were synthesized via hydrothermal route in the presence of Tergitol as a capping agent. The precursors on heating with boron at 1300°C lead to the formation of nanostructures (cubes, rods and pyramids) of lanthanum cerium hexaboride. We have investigated the field emission behaviour of the hexaboride films fabricated by spin coating. It was observed that the pyramidal shaped nanostructures of $La_{0.5}Ce_{0.5}B_6$ shows excellent field emission characteristics with high field enhancement factor of 4502.

In chapter 5, a low temperature route for the synthesis of nanocrystalline chromium diboride which has been further utilized to fabricate chromium boride films. The study focuses on two aspects (1) synthesis of high purity nanocrystalline CrB_2 powder and (2) their application in fabricating chromium boride films. The nanocrystalline chromium diboride powder was obtained by the thermal decomposition of a starting precursor (mixture of chromium acetate and boron powder) which was further used to fabricate chromium boride films via thermal evaporation technique on various substrates (copper,

borosilicate glass and fused silica substrates). The key idea for the stabilization of CrB_2 at low temperature is the in-situ generation of Cr_2O_3 (by decomposition of chromium acetate) which efficiently reacts with elemental boron at 1000°C (~ 500°C lower than the reported temperature of 1500°C). Adsorption of chromium acetate onto boron surface has been carried out in ethanolic medium, which facilitates inter-particle interaction (which is an electrostatic in nature) in the starting precursor (mixture of chromium acetate and boron powder) which is also one of the key factors in lowering the temperature during the thermal decomposition process. Transmission electron microscopy study of the as obtained CrB_2 confirms the formation of nanoparticles of average size (diameter) of ~ 25 nm. The growth patterns of chromium diboride thin films deposited by thermal evaporation on borosilicate glass, fused silica, single crystal Si and Cu substrates has been carried out. It is shown that the adhesion of films is best on Cu, whereas on the other substrates films of thickness > 200 nm is not stable. Scanning electron micrographs reveal that the films on Cu are marginally dense whereas on the other three substrates there is evidence for microporosity, clustering and three dimensional cracks. The as-deposited films on borosilicate glass substrates were amorphous independent of thickness. The films on fused silica, in contrast, crystallized at 60 nm thickness and showed the formation of boron deficient CrB_2. At higher thickness there was evidence for both CrB_2 and the boron deficient Cr_2B_3 or Cr_3B_4 . In the case of films on Si substrate, the presence of both CrB_2 and the boron deficient Cr_2B_3 or Cr_3B_4 is evident. On Cu substrates, up to a thickness of 200 nm only reflections due to the CrB_2 phase are observable. At higher thickness the films consist of both CrB_2 and the boron deficient Cr_2B_3 or Cr_3B_4 phases. Nanoindentation studies reveal strong substrate dependent

mechanical behavior. The hardness of the films is highest on fused silica with a value of 13.5 GPa. The highest hardness achieved on borosilicate glass and Cu substrates was 10 GPa. Interestingly, the Young's modulus value on all the substrates is less than 50% of the bulk value, ranging between 60 and 100 GPa. This has been correlated with presence of microporosity and non-stoichiometry in the films. Spectral transmission studies on the films show that they become opaque on borosilicate glass and fused silica substrates at thicknesses > 150 nm. The reflectance of the Cu substrate is enhanced by 25% at 2500 nm due to the presence of the chromium diboride coatings.

In chapter 6, a new process has been developed for the synthesis of nanocrystalline niobium oxide and niobium diboride using an amorphous niobium precursor obtained via the solvothermal route. On varying the ratio of **niobium precursor to boron** and the reaction conditions, pure phases of nanostructured niobium oxides (Nb_2O_5, NbO_2), niobium diboride (NbB_2) and core-shell nanostructures of $NbB_2@Nb_2O_5$ could be obtained at normal pressure and low temperature of 1300^OC compared to a temperature of 1650^OC normally used. The above borothermal process involves the in situ generation of B_2O_2 to yield either oxide or diboride. The niobium oxides and borides have been characterized in detail by XRD, HRTEM and EDX studies. The core-shell structure has been investigated by XPS depth profiling, EFTEM and EELS (especially to characterize the presence of boron and the shell thickness. The niobium diboride nanorods (with high aspect ratio) show a superconducting transition with the Tc of 6.4 K. In the core-shell $NbB_2@Nb_2O_5$ the superconductivity of NbB_2 is masked by the niobium oxide shell and hence no superconductivity was observed. The above methodology has the benefits of

realizing both oxides and borides of niobium in nanocrystalline form, in high purity and at much lower temperatures.

Chapter 7 describes a hydrothermal route precursor mediated process to obtained nanostructured zirconium hydroxide precursor and its transformation to obtained nanostructured zirconium diborides and metal doped zirconium diborides at considerably low temperature compared to conventional solid state route. In this process, the nanostructured zirconium and metal-zirconium precursors (Metal: Y, Nb and Hf) were heated with boron at low temperature under inert atmosphere (without any flux or additives) to obtain the ZrB_2, $Zr_{0.9}Nb_{0.1}B_2$, $Zr_{0.95}Nb_{0.05}B_2$ nanoparticles, $Zr_{0.95}Y_{0.05}B_2$ cubes and $ZrB_2@MB_2$ (M: Y, Hf) for the first time. This zirconium precursor mediated route leads to zirconium diboride at much lower temperature (~500°C lower than earlier reports). All the phases have been characterized using powder x-ray diffraction, transmission electron microscopic and EDX studies. Further, the preliminary corrosion study by weight loss method have been carried out which indicates all the phases are highly anticorrosive in which only 3 % wt loss in highly concentrated acidic and basic medium represents that the materials can be used in highly anticorrosive medium.

Chapter 8 deals with conclusions and future prospects of the work described above. The thesis has led to the development of low temperature methodologies using nanostructured metal precursors to obtain various morphologies of nanostructured binary and ternary metal borides. The metal precursor of various size and morphology has been obtained using reverse micellar and hydrothermal route. The methods employed have enabled us to lower the reaction temperature by 200 to 650°C in different metal borides. Among many binary metal borides, we have focused on the synthesis of metal diborides

(CrB_2, NbB_2 and ZrB_2) and metal hexaborides (LaB_6, CeB_6). The ternary metal boride of $M_xZr_{1-x}B_2$ (where M= Y,Nb and Hf, x=0.05 and 0.1) and $La_{1-x}Ce_xB_6$ (x= 0.1,0.2,0.3 and 0.5) has also been obtained in pure phases. Thin films of the metal borides have been obtained by spin coating method. The structure and properties of these nanostructures have been analyzed in details and the conclusions will be expressed in this chapter. The field emission studies of field emission properties of all metal hexaboride have shown that the

In annexure-I, we focus on the development of a new route for the synthesis of pure nickel borate nanoparticles using microemulsion mediated process. Nickel borate nanoparticles (25 nm) were synthesized from a precursor (obtained by reverse micellar route) containing both nickel and boron (nickel nitrate and sodium borohydride as starting materials) using CTAB surfactant. Anisotropic nanostructures of nickel borate (a fuel cell electrode) with controlled size and morphology has been synthesized using Tergitol surfactants. Tergitol microemulsions with various co-surfactants (1-butanol,1-hexanol and 1-octanol) have been used to obtain uniform nanorods (dia 3-5 nm, length 25 nm) and nanospindles (dia 30 nm, length 400 nm). A higher chain length of the co-surfactant (1-octanol) leads to more uniform rods rather than spindles (1-butanol). These nanorods show antiferromagnetic behavior with the Néel temperature ranging from 44 to 47 K. Though there is no marked variation in Nėel temperature, the magnetic moment increases drastically with the anisotropy of nanorods (thinner rods) and it has been observed that the nanoparticles offers lower magnetic susceptibility compared to the anisotropic nanostructures of nickel borate.

In annexure II, we have shown the process of fabrication of chromium borate films using e-beam evaporation technique. The growth and optical properties of $CrBO_3$ thin films in the thickness range of 2 to 5 μm deposited by *e*-beam evaporation on to borosilicate glass substrates is reported for the first time. All films were deposited at ambient temperature using CrB_2 as the source material. Electron diffraction studies revealed the low-temperature growth of nanocrystalline $CrBO_3$ films. Raman and FT-IR spectra of the films exhibit signatures of three co-ordinated boron clearly signifying the formation of the borate. The spectral transmission of $CrBO_3$ films shows that films of the order of 2 micron are highly transparent (≈ 80%) in the visible region. The refractive index at 750 nm varies from 1.6 to 1.7 and the band gap is of the order of 2.4 to 2.8 eV. Nanoindentation measurements performed on the films indicate that the films are soft with hardness of the order of 0.5-1GPa.

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