Electrochemical Synthesis of Magnesium Hexaboride by Molten Salt Technique

S. Angappan, 1 N. Kalaiselvi, 2 R. Sudha, 1 and A. Visuvasam 1

1 CSIR-Central Electrochemical Research Institute, Karaikudi 630006, India
2 Department of Physics, Selvam Arts and Science College, Namakkal 637003, India

Correspondence should be addressed to S. Angappan; angs67@gmail.com

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The present work reports electrochemical synthesis of MgB 6 from molten salts using the precursor consists of LiF–B 2 O 3–MgCl 2 . An attempt has been made to synthesize metastable phase MgB 6 crystal by electrolysis method. DTA/TGA studies were made to determine the eutectic point of the melt and it was found to be around 900°C. The electrolysis was performed at 900°C under argon atmosphere, at current density of 1.5A/cm 2. The electrodeposited crystals were examined using XRD, SEM, and XPS. From the above studies, the electrochemical synthesis method for hypothetical MgB 6 from chloro-oxy-fluoride molten salt system is provided. Mechanism for the formation of magnesium hexaboride is discussed.

1. Introduction

Rare earth and alkaline earth metal borides belong to the group of nonoxide type metal-like compounds and have high melting point, high chemical stability, stable specific resistance, low expansion coefficient at certain temperature ranges, diverse magnetic orders, and high neutron absorbability [1, 2]. They have possessed excellent corrosion and wear resistance, chemical inertness, and thermal shock resistance more than that of oxide ceramics [3, 4]. The alkaline earth hexaborides were long thought to be simple polar semiconductors with single particle gap energy of several tenths of an eV and the energy gap is narrow as well as indirect band gap ($\Delta E_g = 0.0150$ Ry).

Electrochemical synthesis of Mg–B system from molten salts is an economic feasible and environmental friendly way for the preparation of different binary phases [5]. Particularly, the Mg–B system was reported early [6, 7] to contain five phases, whereas Serebryakova [8] reported only four phases. Borides can exist as a wide range of compositions and display structural features, which depends strongly on the metal and boron ratio. Markowsky et al. proposed formation of three phases with higher B content as the result of thermal decomposition of MgB 2: (1) MgB 4, (2) unknown, and (3) MgB 12 [9]. However, Duhart reexamined these data and claimed that phase 1 corresponds to MgB 4 and phase 2 to MgB 6 and the formation of MgB 12 (phase 3) was not confirmed [10]. MgB 6 and MgB 4 do not exist as individual phases and obviously are metastable with rather long equilibration times. According to Somsonov et al. [11], Mg–B system has four stable borides: MgB 2, MgB 4, MgB 6, and MgB 12. Mg–B system contains the phases of MgB 2, MgB 4, MgB 6, MgB 12, and MgB 14. So the Mg–B system is known as multiphase system. The aim of the present work is to study whether the thermodynamically unstable MgB 6 [12, 13] could be prepared as thermally stable compound by electrochemical synthesis method.

2. Experimental Procedure

The mixture of the salts LiF (12.95 mol%), B 2 O 3 (22.27 mol%), and MgCl 2 (17.14 mol%) (analytical grade from Merck, India) was taken as an electrolyte in high-density graphite crucible and acts as an electrolyte cell as well as anode for the electrolytic process. The Molybdenum rod of 1 cm diameter fitted to a stainless steel rod is used as cathode. The crucible was filled with the stoichiometric quantities of electrolyte salts, which were dried at 500°C under argon atmosphere. The whole assembly was placed in an inconel reactor, which was kept in an electrical heating furnace with thermocouple. The
experimental setup for the electrosynthesis of magnesium hexaboride is described elsewhere [14–17]. Then the salts were melted slowly under a continuous flow of argon gas. The melt was equilibrated at 900°C for one hour before proceeding electrolysis [15–17]. The bath was pre-electrolyzed to 2.0 V for one hour to remove the impurities and moisture prior to electrolysis. The cathode was centrally positioned at the electrolytic cell. Experiment was carried out at current density of 1.5 A/cm² with the molar ratio of Mg:B as 1:6. After 5 hours of electrolysis the cathode was removed and the deposit was cooled in atmosphere. The deposit was then scraped off and the electrolyte adhering to it was leached with warm 5% HCl solution. Finally washing was done with distilled water for several times, the weight of the deposit was determined, and the nature of the powder was analyzed.

The phase formation and the structural details of the synthesized compound were characterized by X-ray powder diffraction (XRD) using CuKα (λ = 1.541 Å) radiation with 2θ value range of 20 to 90 using PANalytical X’pert powder diffractometer. Differential thermal analysis and thermogravimetric analysis (TGA/DTA) of the reaction mixture was done using Rigaku Thermal—Plus TG 8120 with heating speed 10°C/min in a flow of air. The Fourier transform infrared (FTIR) spectra were recorded in the range of 400 to 4000 cm⁻¹ using Perkin Elmer UK Paragon—500 spectrometer. Scanning electron microscopy (SEM) was employed for the morphological studies using JEOL JSM 3.5 CF Japan make model. UV Visible Spectrophotometer was employed for the absorbance study using JASCO Model 7800 UV Visible Spectrophotometer. Studying the binding energy of boron and magnesium was done using X-ray photoelectron spectroscopy Thermo Scientific UK Multilab 2000.

3. Results and Discussion

Figure 1 presents the powder XRD pattern of the MgB₆ synthesized by molten salt technique. The lattice constant value a = 4.114 Å is determined from the XRD data and is well matched with the reported value (a = 4.115 Å) [18–20] for MgB₆ (JCPDS data card number 08-0421) existing in body centered cubic crystal structure (the space group Pm3m) [20]. But indexing the plans for MgB₆ is difficult because the information on its lattice parameters and structure system is not available in 08-0421. The main building blocks of the MgB₆ structure are B₆ octahedra. Other than MgB₆ some additional traces of MgO are also present at 2θ = 43 and 62.5° due to the partial oxidation of Mg [21]. The crystalline size is found to be 42 nm calculated by using Debye-Scherrer equation as follows:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

where \( k \) is the Scherrer constant usually taken as 0.9, \( \lambda \) is the wavelength characteristics of the Cu-Kα radiation (\( \alpha = 1.5406 \) Å), \( \beta \) is the full width at half-maximum (FWHM) in radians, \( \theta \) is the reflecting angle, and \( D \) is the crystal size.

The TGA/DTA curve for the reaction mixture is shown in Figure 2. The figure showed that the eutectic point of the melt is found to be 820°C. The melt temperature is kept approximately 80°C higher than the eutectic point to reduce the melt viscosity. The LiF is used to increase the fluidity and electrical conductivity of the melt. Its decomposition potential is more cathodic than any other salts chosen. A gradual weight loss observed up to 497°C due to the oxidation of the reactants (2) [22, 23]. MgCl₂ stretches excess Mg and also increases the electrical conductivity of the melt. This excess Mg combines with O forming MgO (from residual B₂O₃). The formation of 2MgCl₂·3B₂O₃ is due to the solid-state reaction between residual B₂O₃ and MgCl₂ turn into molten state (melting point of MgCl₂: 708°C) is confirmed by an exothermic peak at 761°C. Finally, the reactants can be oxidized thoroughly at 761°C [24]. Further weight loss observed up to 1000°C is responsible for the transformation of the reactants into desired product. In the DTA curve, a sharp exothermic spike
The FTIR spectrum of MgB$_6$ is shown in Figure 5. The O–H stretching vibrations of water crystallization are present at 3743 and 3413 cm$^{-1}$, respectively. The absorption at 2225 cm$^{-1}$ is assigned to O–H stretching vibration of cluster of water molecules of crystallization, respectively. The characteristic peak of Mg–B is observed at 1642 cm$^{-1}$ [32]. Longitudinal optic mode frequency of Mg–O is observed at 705 cm$^{-1}$; this MgO as impurity phases is also observed in the XRD pattern. The bending vibration for MgB$_6$ is observed at 437 cm$^{-1}$. The bending mode of Mg–B of BO$_4$ anion is assigned to 499 cm$^{-1}$. The asymmetric stretching vibration of Mg–B of BO$_4$ anion is observed at 1021 cm$^{-1}$. The asymmetric stretching vibration of B–O bond of trigonal BO$_3$ units is observed at 1367 cm$^{-1}$. The frequencies observed in the spectrum are in good agreement with the reported values [33, 34].

The mechanism of hexaboride formation was proposed by many authors [12, 14–17, 37–47]. According to Li and Jin, the negative charged boron atoms and the positive charged alkaline earth metal atoms form complexes of M$^{2+}$ metal cation and B$_6$$^{2–}$ dianion due to electrostatic attraction. They also suggested that the metal cations M$^{2+}$ have definite role on stabilizing the B$_6$$^{2–}$ dianion [12]. Kaptay and Kuznetsov also reported that the boron components are dissolved in ionic form in the melt, to form boride phase on the cathode joint with metal cations [37]. Jose et al. reported the “unstable stoichiometric way” for the deposition of Barium hexaboride [14]. We reported earlier that the electrolytically dissociated metal and B ions deposit on the cathode as CeB$_6$ and SmB$_6$, respectively [15, 16]. We also reported in our earlier study on CaB$_6$ that the calcium and boron are reduced at the cathode to form submicron sized crystals [17]. As reported by Chen et al. [38], the formation of MgB$_6$ at 900°C as one of the secondary phases along with MgB$_4$ due to Mg deficiency of Mg at this temperature resulted in Mg deficiency in situ Cu doping of MgB$_2$. The commonly accepted mechanism of boron deposition in molten salts is a single-step three-electron electrochemical reaction [39–43]. Gloor et al. investigated the multiexciton bound state of molecules in divalent hexaborides. They proposed that the larger energy gain per one electron-hole pair decreases the semiconducting gap and produced intermediate phase. This may be the reason for the formation of intermediate phase MgB$_6$ [44]. Li et al. described the diffusion of Mg vapour into boron creating a complex of Mg–B supersaturated solution, encompassing the formation of nonequilibrium MgB$_6$ [45]. Lee et al. and J.Q. Li also authenticated with S. Li [45] and postulated that the path of the reaction of supersaturated Mg–B cluster complex via spinodal decomposition leads to the formation of hypothetical phase MgB$_6$ [46, 47].
4. Conclusion

In summary, the electrochemical synthesis of hypothetical magnesium hexaboride by molten salt technology is presented. Various mechanisms for the formation of magnesium hexaboride are discussed. It is believed that the supersaturated MgB$_6$ cluster complex is postulated for the metastable magnesium hexaboride compound. Further experimental evidence is more needed to explore the thermodynamically unstable magnesium hexaboride.
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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