Research Article

Electrochemical Synthesis of Magnesium Hexaboride by Molten Salt Technique

S. Angappan,¹ N. Kalaiselvi,² R. Sudha,¹ and A. Visuvasam¹

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; ang67@gmail.com

Received 24 March 2014; Revised 23 May 2014; Accepted 26 May 2014; Published 31 August 2014

The present work reports electrochemical synthesis of MgB₆ from molten salts using the precursor consists of LiF–B₂O₃–MgCl₂. An attempt has been made to synthesize metastable phase MgB₆ 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 1.5 A/cm². The electrodeposited crystals were examined using XRD, SEM, and XPS. From the above studies, the electrochemical synthesis method for hypothetical MgB₆ 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 absorba-

ibilty [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 semicon-
ductors 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 decom-
position of MgB₂: (1) MgB₆, (2) unknown, and (3) MgB₁₂ [9]. However, Duhart reexamined these data and claimed that phase 1 corresponds to MgB₆ and phase 2 to MgB₁₂, and the formation of MgB₁₂ (phase 3) was not confirmed [10]. MgB₆ and MgB₁₂ 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: MgB₂, MgB₄, MgB₆, and MgB₁₂. Mg–B system contains the phases of MgB₂, MgB₄, MgB₆, MgB₁₂, and Mg₂B₁₄. So the Mg–B system is known as multiphase system. The aim of the present work is to study whether the thermodynamically unstable MgB₆ [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%), B₂O₃ (22.27 mol%), and MgCl₂ (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 preelectrolyzed at 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 determined, and then the nature of the powder was analyzed. The melt was equilibrated at 900 °C in the heating process. These reactants whether in solid or gaseous state play a crucial role in determining the shape of the final product. Further, this weight gain is mainly 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

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, λ is the wavelength characteristics of the Cu-Kα radiation (λ = 1.5406 Å), β is the full width at half-maximum (FWHM) in radiations, θ 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 may be due to the removal of moisture and inbound water associated with the salts. The weight gain which is observed up to 761 °C from 497 °C, due to B₂O₃, begins to turn into liquid (melting point 450 °C) in the heating process. These reactants whether in the liquid or gaseous state play a crucial role in determining the shape of the final product. Further, this weight gain is mainly 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

![Figure 1: XRD pattern for MgB₆.](image1)

![Figure 2: TG/DTA curve for MgB₆.](image2)
Figure 3: DSC curve for MgB₆.

is observed at 742°C which may also be verified by confirming this process. This is gratuitous to the DSC curve (Figure 3) at 745°C; a sharp exothermic spine is observed that the heat of decomposition of salts is about 513.3 J/g.

The reaction was carried out for MgB₆ in MgCl₂–B₂O₃–LiF system; the main chemical reactions are

\[ 2\text{MgCl}_2 + 3\text{B}_2\text{O}_3 \rightarrow 2\text{MgCl}_2 \cdot 3\text{B}_2\text{O}_3 \]  

(2)

\[ 2\text{MgCl}_2 \cdot 3\text{B}_2\text{O}_3 \rightarrow \text{MgB}_6 + \text{MgO} + 4\text{O}_2 (g) + 2\text{Cl}_2 (g) \uparrow \]  

(3)

The overall reaction is

\[ 2\text{MgCl}_2 + 3\text{B}_2\text{O}_3 \rightarrow \text{MgB}_6 + \text{MgO} + 4\text{O}_2 + 2\text{Cl}_2 (g) \uparrow \]  

(4)

Trace amount of the unreacted intermediate MgO was present in the synthesized compound as 0.6% and the remaining 99.4% was MgB₆ as depicted from XRD pattern.

The XPS spectrum for B is shown in Figure 4(a). The higher binding energy value for B is exists at 198.6 eV. This reflects contributions from both trigonal BO₃ and tetrahedral BO₄ groups. The electron transfer would come from trigonal B is to B–O σ⁺ orbital and from the unfilled tetrahedral B 2p orbital to B–O σ⁺ [25, 26]. This B is → σ⁺ resonance as expected for sp²-bonded boron incorporated in the crystal [27]. Figure 4(b) shows the Mg 1s spectra for MgB₆ at 1314 eV revealed that the auger spectral distribution over an extruded energy range far from the threshold; there is an extra energy for Mg rich compound [28]. Figure 4(c) shows the O 1s spectrum for MgB₆ existing at 544 eV. This may be due to the core-hole Rydberg states containing O 1s → σ⁺ resonance [29, 30]. Figure 4(d) shows C is spectrum at 296 eV and reveals energy transitions between a carbon core level and an antibonding π⁺ molecular orbital [31]. The surface is contaminated due to exposure to air during the processing of the sample.

The Mg²⁺ cations in MgB₆ complex species have C₃ᵥ pyramidal structures interacting with a planar hexagonal B₆²⁻ dianion. The bonding between these two may be due the electrostatic attraction [12].
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.

Acknowledgments

The authors would like to thank the Director of CSIR-CECRI for his keen interest and encouragement and staff of EMP Division for their support. S. Angappan acknowledges the Council of Scientific and Industrial Research (CSIR), India, for providing the financial assistant to the project EMPOWER (OLP 0060).

References

[1] K. Segawa, A. Tomita, K. Iwashita, M. Kasaya, T. Suzuki, and S. Kunii, "Electronic and magnetic properties of heavy rare-earth hexaboride single crystals," Journal of Magnetism and Magnetic Materials, vol. 104–107, no. 2, pp. 1233–1234, 1992.

[2] C. L. Perkins, M. Trenary, T. Tanaka, and S. Otani, "X-ray photoelectron spectroscopy investigation of the initial oxygen adsorption sites on the LaB6(100) surface," Surface Science, vol. 423, no. 1, pp. L222–L228, 1999.

[3] C. Chen, W. Zhou, and L. Zhang, "Oriented structure and crystallography of directionally solidified LaB6-ZrB2 eutectic," Journal of the American Ceramic Society, vol. 81, no. 1, pp. 237–240, 1998.

[4] S.-Q. Zheng, Z.-D. Zou, G.H. Min, H. Yu, J. Han, and W. Wang, "Synthesis of strontium hexaboride powder by the reaction of strontium carbonate with boron carbide and carbon," Journal of Materials Science Letters, vol. 21, no. 4, pp. 313–315, 2002.

[5] G. Kaptay, I. Sytchev, M. S. Yaghmaee, A. Kovacs, E. Cserta, and M. Ark, "Classification of borides," Journal of the Less-Common Metals, vol. 67, no. 2, pp. 499–503, 1979.

[6] T. Y. Kosolapova, Ed., Preparation and Application of Refractory Compounds, Metallurgiya, Moscow, Russia, 1986.

[7] T. I. Serebryakovka, V. A. Neronov, and P. D. Peshev, High Temperature Borides, Metallurgiya, Chelyabinsk, Russia, 1991.

[8] T. A. Serebryakovka, "Oxidation of aluminum in molten boron carbide. II. Kinetic aspects," Journal of Alloys and Compounds, vol. 133, no. 4, pp. 319–324, 1995.

[9] P. Duhart, “The borides of magnesium and aluminum,” Annali di Chimica, vol. 7, pp. 339–365, 1962.

[10] G. V. Samsonov, T. I. Serebriakovka, and V. A. Neronov, Borides, Atomizdat, Moscow, Russia, 1975 (Russian).

[11] Q. S. Li and Q. Jin, “Theoretical study on the acidity of the pyramidal MB6 (M = Be, Mg, Ca, and Sr) clusters,” The Journal of Physical Chemistry A, vol. 107, no. 39, pp. 7869–7873, 2003.

[12] G. K. Moiseev and A. L. Ivanovskii, "Thermodynamic properties and thermal stability of magnesium borides," Inorganic Materials, vol. 41, no. 10, pp. 1061–1066, 2005.

[13] T. P. Jose, L. Sundar, L. J. Berchmans, A. Visuvasam, and S. Angappan, "Electrochemical synthesis and characterization of BaB6 from molten melt," Journal of Mining and Metallurgy B: Metallurgy, vol. 45, no. 1, pp. 101–109, 2009.

[14] K. Amalajyothi, L. J. Berchmans, S. Angappan, and A. Visuvasam, "Electrosynthesis of cerium hexaboride by the molten salt technique," Journal of Crystal Growth, vol. 310, no. 14, pp. 3376–3379, 2008.

[15] L. J. Berchmans, A. Visuvasam, S. Angappan, and A. K. Suri, "Electrosynthesis of samarium hexaboride using tetra borate melt," Ionics, vol. 16, no. 9, pp. 833–838, 2010.

[16] S. Angappan, M. Helan, A. Visuvasam, L. J. Berchmans, and V. Ananth, "Electrolytic preparation of CaB6 by molten salt technique," Ionics, vol. 17, no. 6, pp. 527–533, 2011.

[17] I. Popov, N. Baadji, and S. Sanvito, "Magnetism and antiferroelectricity in MgB6," Physical Review Letters, vol. 108, no. 10, Article ID 107205, 2012.

[18] A. L. Ivanovskii, "Superconducting MgB2 and related compounds: synthesis, properties and electronic structure," Russian Chemical Reviews, vol. 70, pp. 717–734, 2001.

[19] V. G. Pol, S. V. Pol, I. Felner, and A. Gedanken, "Critical current density in the MgB2 nanoparticles prepared under autogenic pressure at elevated temperature," Chemical Physics Letters, vol. 433, no. 1–3, pp. 115–119, 2006.

[20] M. Zhang, X. Wang, X. Zhang et al., "Direct low-temperature synthesis of RB6 (R= Ce, Pr, Nd) nanocubes and nanoparticles," Journal of Solid State Chemistry, vol. 182, no. 11, pp. 3098–3104, 2009.

[21] P. Peshev, "A thermodynamic analysis of lanthanum hexaboride crystal preparation from aluminum flux with the use of compound precursors," Journal of Solid State Chemistry, vol. 133, no. 1, pp. 237–242, 1997.

[22] J. Ma, Y. Du, M. Wu et al., "A simple inorganic-solvent-thermal route to nanocrystalline niobium diboride," Journal of Alloys and Compounds, vol. 468, no. 1-2, pp. 473–476, 2009.

[23] A. M. Duffin, C. P. Schwartz, A. H. England, J. S. Uejio, D. Prennegerst, and R. J. Saykally, "pH-dependent x-ray absorption spectra of aqueous boron oxides," Journal of Chemical Physics, vol. 134, no. 15, Article ID 154503, 2011.

[24] M. E. Fleet and S. Muthupari, "Boron K-edge XANES of borate and borosilicate minerals," American Mineralogist, vol. 85, no. 7-8, pp. 1009–1021, 2000.

[25] J. L. Blackburn, Y. Yan, C. Engrtrakul et al., "Synthesis and characterization of boron-doped single-wall carbon nanotubes produced by the laser vaporization technique," Chemistry of Materials, vol. 18, no. 10, pp. 2558–2566, 2006.

[26] S. Altieri, L. H. Tjeng, F. C. Voogt, T. Hibma, O. Rogojanu, and G. A. Sawatzky, "Charge fluctuations and image potential at oxide-metal interfaces," Physical Review B, vol. 66, no. 15, Article ID 154332, pp. 1554321–1554326, 2002.

[27] S. Sorensen, T. Tanaka, R. Feifel et al., "Application of a atomic relaxation model for the interpretation of O1s to Rydberg excited Auger electron spectra of molecular oxygen," Chemical Physics Letters, vol. 398, no. 1–3, pp. 168–174, 2004.

[28] R. Feifel, T. Tanaka, M. Kitajima et al., "Probing the valence character of O1s → Rydberg excited O2 by participant Auger decay measurements and partial ion yield spectroscopy following x-ray absorption," The Journal of Chemical Physics, vol. 126, Article ID 174304, 2007.

[29] A. Talapatra, S. K. Bandyopadhyay, P. Sen, P. Barat, S. Mukherjee, and M. Mukherjee, "X-ray photoelectron spectroscopy...
studies of MgB$_2$ for valence state of Mg,” *Physica C: Superconductivity*, vol. 419, no. 3-4, pp. 141–147, 2005.

[32] S. N. Kumar, S. Das, C. Bernhard, and G. D. Varma, “Effect of graphene oxide doping on superconducting properties of bulk MgB$_2$,” *Superconductor Science and Technology*, vol. 26, no. 9, Article ID 095008, 2013.

[33] K. Nakamato, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, NY, USA, 5th edition, 1977.

[34] S. D. Ross, *Inorganic Infrared and Raman Spectra*, McGraw Hill, London, UK, 1972.

[35] X. Chen, T. Xia, M. Wang, W. Zhao, and T. Liu, “Microstructural transformation during combustion synthesis of MgB$_2$ superconductor,” *Physica C: Superconductivity and its Applications*, vol. 454, no. 1-2, pp. 38–42, 2007.

[36] R. G. Abhilash Kumar, K. Vinod, R. P. Aloysius, and U. Syamaprasad, “A simple and inexpensive method for rapid synthesis of MgB$_2$ superconductor,” *Materials Letters*, vol. 60, no. 28, pp. 3328–3331, 2006.

[37] G. Kaptay and S. A. Kuznetsov, “Electrochemical synthesis of refractory borides from molten salts—review paper,” *Plasmas & Ions*, vol. 2, pp. 45–56, 1999.

[38] S. K. Chen, M. Majoros, J. L. MacManus-Driscoll, and B. A. Glowacki, “In situ and ex situ Cu doping of MgB$_2$,” *Physica C: Superconductivity and its Applications*, vol. 418, no. 3-4, pp. 99–106, 2005.

[39] R. Thompson, “The chemistry of metal borides & related compounds,” in *Progress in Boron Chemistry*, R. J. Brotherton and H. Steinberg, Eds., vol. 2, pp. 178–230, Pergamon Press, Oxford, UK, 1970.

[40] P. R. Davis, M. A. Gesley, G. A. Schwind, L. W. Swanson, and J. J. Hutta, “Comparison of thermionic cathode parameters of low index single crystal faces of LaB$_6$, CeB$_6$ and PrB$_6$,” *Applied Surface Science*, vol. 37, no. 4, pp. 381–394, 1989.

[41] S. V. Meschel and O. J. Kleppa, “Standard enthalpies of formation of some borides of Ce, Pr, Nd and Gd by high-temperature reaction calorimetry,” *Journal of Alloys and Compounds*, vol. 226, no. 1-2, pp. 243–247, 1995.

[42] G. Balakrishnan, M. R. Lees, and D. M. K. Paul, “Growth of large single crystals of rare earth hexaborides,” *Journal of Crystal Growth*, vol. 256, no. 1-2, pp. 206–209, 2003.

[43] C. Y. Zou, Y. M. Zhao, and J. Q. Xu, “Synthesis of single-crystalline CeB$_6$ nanowires,” *Journal of Crystal Growth*, vol. 291, no. 1, pp. 112–116, 2006.

[44] T. A. Gloor, M. E. Zhitomirsky, and T. M. Rice, “Multie exciton molecules in the hexaborides,” *European Physical Journal B*, vol. 21, no. 4, pp. 491–497, 2001.

[45] S. Li, O. Prabhakar, T. T. Tan et al., “Intrinsic nanostructural domains: possible origin of weaklinkless superconductivity in the quenched reaction product of Mg and amorphous B,” *Applied Physics Letters*, vol. 81, no. 5, pp. 874–876, 2002.

[46] S. Lee, H. Mori, T. Masui, Y. Eltsev, A. Yamamoto, and S. Tajima, “Growth, structure analysis and anisotropic superconducting properties of MgB$_2$ single crystals,” *Journal of the Physical Society of Japan*, vol. 70, no. 8, pp. 2255–2258, 2001.

[47] J. Q. Li, L. Li, Y. Q. Zhou, Z. A. Ren, G. C. Che, and Z. X. Zhao, “Structural features, stacking faults, and grain boundaries in MgB$_2$ superconducting materials,” http://arxiv.org/abs/cond-mat/0104350.