

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; angs67@gmail.com

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

Academic Editor: Sarkarainadar Balamurugan

Copyright © 2014 S. Angappan et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The present work reports electrochemical synthesis of MgB_6 from molten salts using the precursor consists of $\text{LiF-B}_2\text{O}_3\text{-MgCl}_2$. 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 1.5 A/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

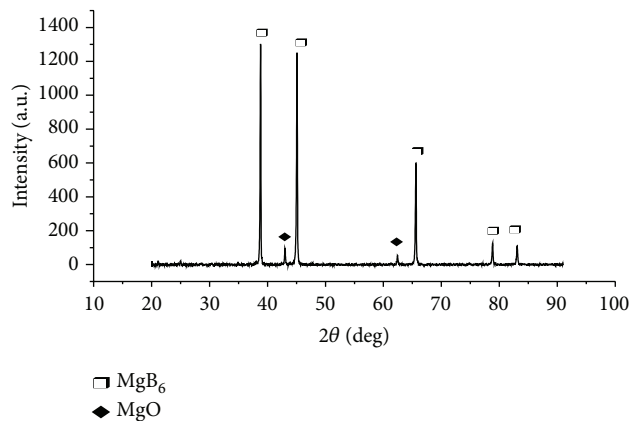
Rare earth and alkaline earth metal borides belong to the group of nonoxide type metal-like compounds and have high melting point, high chemical stability, stable specific resistance, low expansion coefficient at certain temperature ranges, diverse magnetic orders, and high neutron absorptivity [1, 2]. 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 ($\Delta E_g = 0.0150\text{ Ry}$).

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_6 , (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 Mg_2B_{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_2O_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

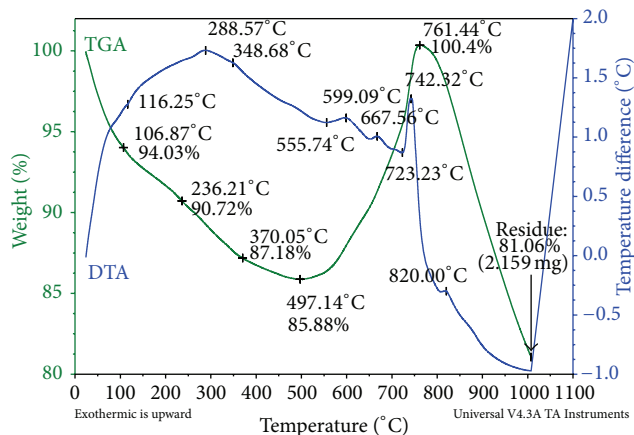
FIGURE 1: XRD pattern for MgB₆.

experimental setup for the electro-synthesis 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 ($\lambda = 1.541 \text{ \AA}$) 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 20°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 $a = 4.114 \text{ \AA}$ is determined from the XRD data and is well matched with the reported value ($a = 4.115 \text{ \AA}$) [18–20] for MgB₆ (JCPDS data card number 08-0421) existing in body centered cubic crystal structure (the space group Pm3m)

FIGURE 2: TG/DTA curve for MgB₆.

[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 $2\theta = 43$ 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:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where k is the Scherrer constant usually taken as 0.9, λ is the wavelength characteristics of the Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$), 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

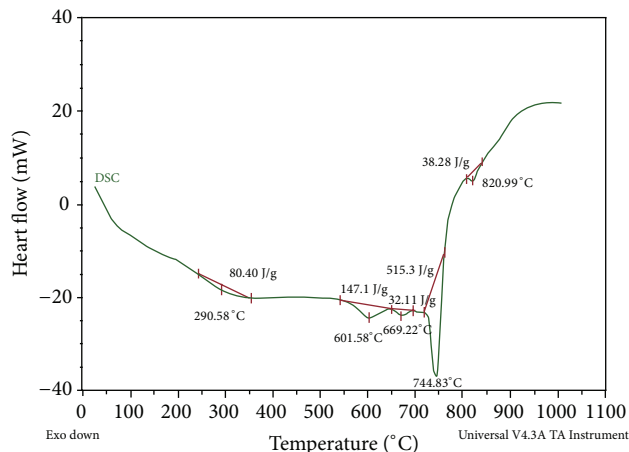
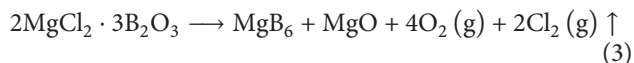


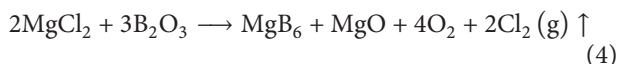
FIGURE 3: DSC curve for MgB_6 .

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 MgB_6 in $\text{MgCl}_2\text{-B}_2\text{O}_3\text{-LiF}$ system; the main chemical reactions are



The overall reaction is



Trace amount of the unreacted intermediate MgO was present in the synthesized compound as 0.6% and the remaining 99.4% was MgB_6 as depicted from XRD pattern.

The XPS spectrum for B 1s is shown in Figure 4(a). The higher binding energy value for B 1s exists at 198.6 eV. This reflects contributions from both trigonal BO_3 and tetrahedral BO_4 groups. The electron transfer would come from trigonal B 1s to $\text{B-O } \sigma^*$ orbital and from the unfilled tetrahedral B 2p orbital to $\text{B-O } \sigma^*$ [25, 26]. This B 1s $\rightarrow \sigma^*$ resonance as expected for sp^2 -bonded boron incorporated in the crystal [27]. Figure 4(b) shows the Mg 1s spectra for MgB_6 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 MgB_6 existing at 544 eV. This may be due to the core-hole Rydberg states containing O 1s $\rightarrow \sigma^*$ resonance [29, 30]. Figure 4(d) shows C 1s 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 Mg^{2+} cations in MgB_6 complex species have C_{6v} pyramidal structures interacting with a planar hexagonal B_6^{2-} dianion. The bonding between these two may be due the electrostatic attraction [12].

The FTIR spectrum of MgB_6 is shown in Figure 5. The O-H stretching vibrations of water crystallization are represent 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 SEM image of the sample is shown in Figure 6. The microstructure indicates that the particle diameters are in the range $4\text{-}8\ \mu\text{m}$. From the microstructure, the molten regions are clearly visible, which give the clear indication of MgB_6 formation. The white regions in SEM represent the impurity phase MgO present in the sample [35, 36]. The present study reveals the formation of MgB_6 phase as cubic crystal structure.

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 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 the volatile nature of Mg at this temperature resulted in Mg deficiency on 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].

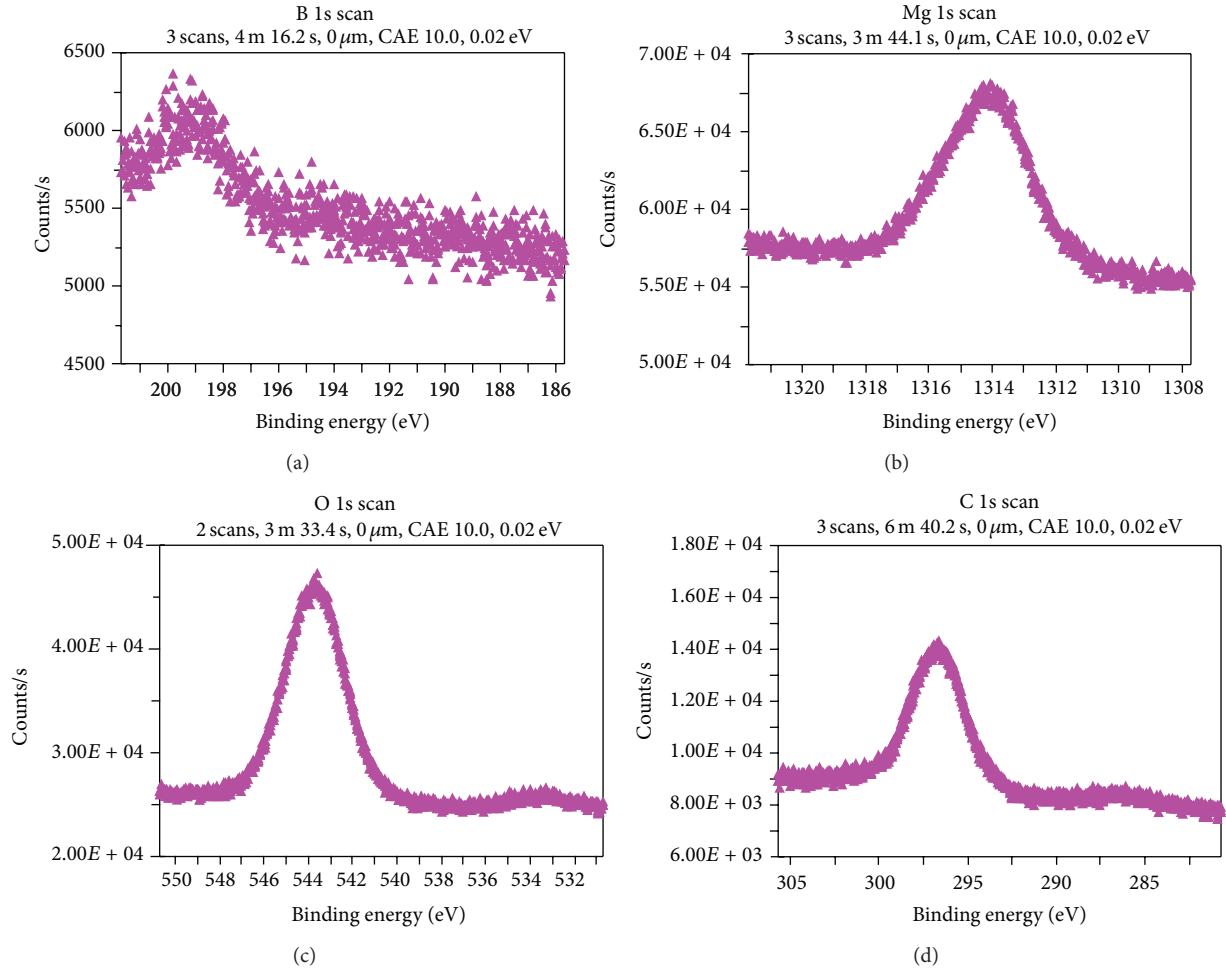


FIGURE 4: XPS spectra for (a) B 1s, (b) Mg 1s, (c) O 1s, and (d) C 1s.

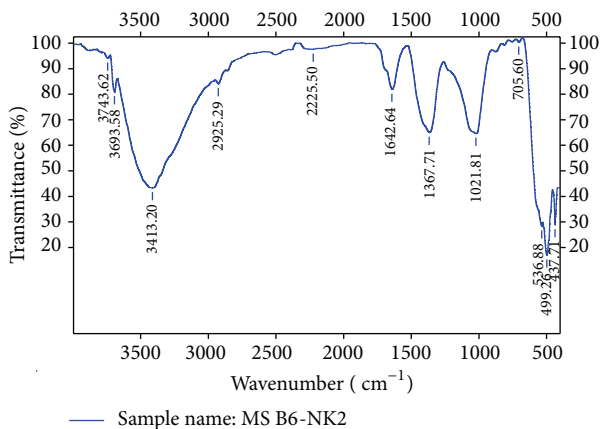


FIGURE 5: FTIR spectrum of MgB_6 .

4. Conclusion

In summary, the electrochemical synthesis of hypothetical magnesium hexaboride by molten salt technology is presented. Various mechanisms for the formation of magnesium

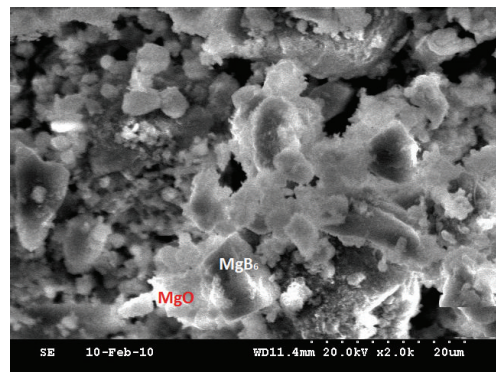


FIGURE 6: SEM image of MgB_6 .

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, in *Proceedings of the 6th International Symposium on Molten Salt Chemistry and Technology*, p. 168, Shanghai, China, 2001.
- [6] T. Y. Kosolapova, Ed., *Preparation and Application of Refractory Compounds*, Metallurgiya, Moscow, Russia, 1986.
- [7] T. I. Serebryakova, V. A. Neronov, and P. D. Peshev, *High Temperature Borides*, Metallurgiya, Chelyabinsk, Russia, 1991.
- [8] T. A. Serebryakova, "Classification of borides," *Journal of the Less-Common Metals*, vol. 67, no. 2, pp. 499–503, 1979.
- [9] L. Markowsky, Y. Kondrashevsky, and G. Kaputovskaya, "The composition and the chemical properties of magnesium borides," *Zhurnal Organicheskoi Khimii*, vol. 25, p. 433, 1955.
- [10] P. Duhart, "The borides of magnesium and aluminium," *Annali di Chimica*, vol. 7, pp. 339–365, 1962.
- [11] G. V. Samsonov, T. I. Serebriakova, and V. A. Neronov, *Borides*, Atomizdat, Moscow, Russia, 1975 (Russian).
- [12] Q. S. Li and Q. Jin, "Theoretical study on the aromaticity 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.
- [13] 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.
- [14] 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.
- [15] 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.
- [16] L. J. Berchmans, A. Visuvasam, S. Angappan, C. Subramanian, and A. K. Suri, "Electrosynthesis of samarium hexaboride using tetra borate melt," *Ionics*, vol. 16, no. 9, pp. 833–838, 2010.
- [17] 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.
- [18] I. Popov, N. Baadji, and S. Sanvito, "Magnetism and antiferroelectricity in MgB₆," *Physical Review Letters*, vol. 108, no. 10, Article ID 107205, 2012.
- [19] S. V. Okatov, A. L. Ivanovskii, Yu. E. Medvedeva, and N. I. Medvedeva, "The electronic band structures of superconducting MgB₂ and related borides CaB₂, MgB₆ and CaB₆," *Physica Status Solidi B*, vol. 225, pp. R3–R5, 2001.
- [20] A. L. Ivanovskii, "Superconducting MgB₂ and related compounds: synthesis, properties and electronic structure," *Russian Chemical Reviews*, vol. 70, pp. 717–734, 2001.
- [21] 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.
- [22] 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.
- [23] 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.
- [24] 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.
- [25] A. M. Duffin, C. P. Schwartz, A. H. England, J. S. Uejio, D. Prendergast, 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.
- [26] 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.
- [27] J. L. Blackburn, Y. Yan, C. Engtrakul 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.
- [28] S. Altieri, L. H. Tjeng, F. C. Voogt, T. Hibma, O. Rogojuanu, and G. A. Sawatzky, "Charge fluctuations and image potential at oxide-metal interfaces," *Physical Review B*, vol. 66, no. 15, Article ID 155432, pp. 1554321–1554326, 2002.
- [29] S. Sorensen, T. Tanaka, R. Feifel et al., "Application of an 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.
- [30] R. Feifel, T. Tanaka, M. Kitajima et al., "Probing the valence character of O 1s → 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.
- [31] 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. Nakamoto, *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, "Multiexciton 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>.