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Possibility of synthesizing lanthanum hexaboride using vacuum-free electric arc method

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This paper presents the results of experimental studies on the development of scientific and technical foundations for the method of synthesizing lanthanum hexaboride (LaB_6) using atmospheric plasma of a direct current arc discharge. The quantitative and qualitative composition of the synthesis product was determined using the results of X-ray diffractometry. The morphology and particle size of the resulting powder material based on lanthanum hexaboride were determined using the results of scanning electron microscopy.

Keywords: lanthanum hexaboride, arc reactor, vacuum-free method, X-ray phase analysis, scanning electron microscopy.

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Lanthanum hexaboride is a refractory compound consisting of a rare earth element (lanthanum) and a non-metallic element (boron). Materials based on lanthanum hexaboride are characterized by high strength, hardness, and electrical and thermal conductivity levels; a low coefficient of linear thermal expansion; and a low electron work function [1]. Therefore, lanthanum hexaboride finds wide application in aerospace, electronic, and medical technology; owing to its low electron work function, it is also used often in electron microscopy [2]. The combination of their properties and wide application possibilities of materials based on lanthanum hexaboride have generated great research interest in the development of methods for its synthesis. Several different methods for production of single-crystal and polycrystalline LaB_6 are currently known. The key of them are mechanochemical synthesis and borothermic reduction [3–9]. However, LaB_6 powders produced by known methods are normally characterized by a low degree of purity, a relatively large particle size, a low sintering activity, and, importantly, high cost; it is also hard to control the synthesis process, and the process cycle is rather lengthy. Plasma arc synthesis is one of the possible solutions to the problem of LaB_6 production [10–12]. Its important advantage is that a wide range of reaction zone temperatures is achieved within a short time. However, methods based on this principle have several known disadvantages, such as contamination of synthesis products by the electrode material, the need to use expensive vacuum systems, and a wide distribution of particle sizes (due to a significant temperature gradient). It is known that the electric arc method may be implemented in open air due to the effect of self-shielding of the reaction zone by CO and CO_2 gases formed in the process of arcing in the discharge gap between graphite electrodes in air. This approach makes the procedure and equipment significantly simpler and is suitable for synthesis of certain carbides, borides, and carbon nanostructures [13,14], but has not yet been used for synthesis of crystalline phases in a system with lanthanum and boron.

hexaboride were carried out using a proprietary plasma arc reactor [15]. Its main elements are a DC source and graphite electrodes. In the standard configuration, a graphite rod 8 mm in diameter serves as an anode and a graphite crucible with an internal diameter of 30 mm is used as a cathode. A smaller graphite crucible with a graphite lid with an internal diameter of 10 mm is positioned in the cavity of the larger crucible. A mixture of lanthanum oxide La_2O_3 powder (chemically pure, „Redkii metall") and amorphous boron (analytical grade, „Ferus") is poured into the cavity of the smaller crucible. The mass ratio of $La_2O_3 : B = 2.153 : 1$ was chosen in accord with the known equation of borothermic reduction of lanthanum oxide and previous experience with other batch compositions. The powders were mixed in a Reatsch PM100 planetary ball mill at 400 rpm for 30 min.

The discharge circuit current strength and the arc discharge duration are the significant and adjustable parameters of the arc reactor. Experiments with the discharge circuit current strength varying from 50 to 200 A and the exposure duration varying from 15 to 75 s were performed. An arc discharge was ignited by bringing the anode into brief contact with the graphite lid and shifting it away to form a 0.5−1.0 mm discharge gap. Following a specified arc processing time, the crucibles were cooled to room temperature, and the synthesis product was removed, ground in an agate mortar, and sent for subsequent analysis. The obtained powder material was examined by X-ray diffractometry (Shimadzu XRD7000s, CuK_α radiation). Qualitative X-ray phase analysis was carried out using the PDF4+ structural database, while the Powder Cell 2.4 software package and

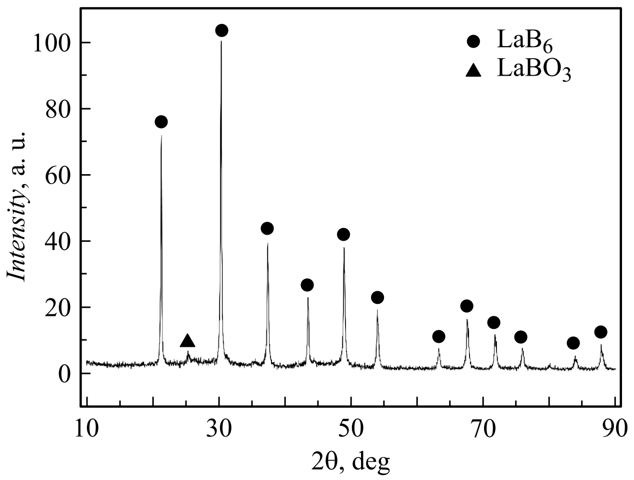

Figure 1. X-ray diffraction pattern of the synthesis product based on lanthanum hexaboride.

a well-known technique based on the integrated intensity of diffraction maxima were utilized in quantitative analysis. The morphology of particles of the synthesis product was examined using a Tescan Vega 3 SBU scanning electron microscope fitted with an Oxford X-Max-50 energy-dispersive spectroscopy (EDS) detector with a Si/Li crystal.

Figure 1 presents the X-ray diffraction pattern for one of the obtained powder synthesis products (synthesis parameters: current strength, 200 A; arcing time, 75 s; mass ratio of the batch components, La_2O_3:B = 2.153:1). With such parameters of the arc reactor, conditions for the formation of an autonomous gas environment with self-shielding and temperatures suitable for synthesis of crystalline phases of lanthanum hexaboride (up to $1600-2000\,^{\circ}C$) are established simultaneously. If the current strength or the process duration are reduced, the desired phase of lanthanum hexaboride is not dominant in the synthesis product. With the recommended parameters, the energy intensity of the process reaches 300 kJ/g (by batch mass).

According to the results of quantitative and qualitative X-ray phase analysis, the typical diffraction pattern features a cubic phase of lanthanum hexaboride with lattice parameter $d_{100} = 4.16 \pm 0.02$ Å(98.3 %) and an orthorhombic phase of lanthanum borate $LaBO_3$ (1.7 %). The result remained unchanged when the experiment was repeated several (up to 10) times in order to evaluate the repeatability and produce material for future sintering experiments.

Figure 2 presents the scanning electron microscopy data for the obtained synthesis product. Particles consisting of individual grains and agglomerated particles characterized by acute and rounded outlines may be identified. Lanthanum hexaboride crystals $\sim 10\,\mu m$ in size are seen in certain regions (Fig. 2, *a*). The bulk of particles identified in scanning electron microscope images are no larger than $\sim 5-6\,\mu m$ in size. The particle size distribution is shown in Fig. 2, *b*.

The reported data provide the first experimental confirmation of feasibility of lanthanum hexaboride powder synthesis with the use of a vacuum-free electric arc method. According to the results of X-ray phase analysis, the developed method allows one to obtain powders with a dominant LaB_6 phase with micrometer particles and a purity of 98.3 %. The energy intensity of the process is up to 300 kJ/g (by batch). In future research, we plan to refine mass and energy balances, enhance product purity, increase the batch mass processed in a single reactor cycle, and evaluate the characteristics of the obtained material in comparison with other methods.

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Conflict of interest

The authors declare that they have no conflict of interest.

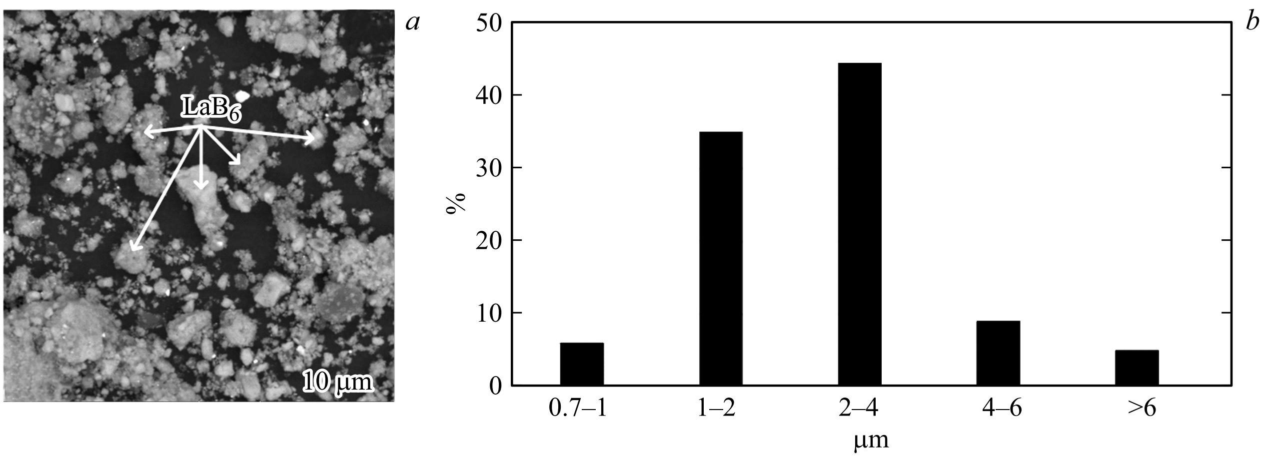

Figure 2. Typical scanning electron microscopy results for synthesis products (*a*) and particle size distribution (*b*).

References

[1] Z. Li, Y. Ou, P. La, Y. Shi, J. Rare Earths, **36**, 623 (2018). DOI: 10.1016/j.jre.2018.01.003
[2] J.M.D. Kowalczyk, M.R. Hadmack, E.B. Szarmes, J.M.J. Madey, Int. J. Thermophys., **35**, 1538 (2014). DOI: 10.1007/s10765-014-1712-3
[3] B. Lihong, Wurentuya, W. Wei, O. Tegus, Mater. Charact., **97**, 69 (2014). DOI: 10.1016/j.matchar.2014.08.011
[4] E.N. Kablov, N.E. Shchegoleva, Yu.E. Lebedeva, P.L. Zhuravleva, M.L. Vaganova, A.S. Chainikova, Glass Ceram., **80** (1–2), 58 (2023). DOI: 10.14489/glc.2023.02.pp.027-041
[5] L.V. Razumova, *Analiz osobennostei sinteza i razrabotka prakticheskikh rekomendatsii polucheniya i ispol'zovaniya nanorazmernogo poroshka geksaborida lantana*, Candidate's Dissertation in Engineering (S.-Peterb. Politekh. Univ., SPb., 2021) (in Russian).
[6] D.O. Chukhvantsev, E.S. Filatov, N.I. Shurov, D.A. Rozhentsev, Inorg. Mater., **57** (1), 14 (2021). DOI: 10.1134/S0020168521010039.
[7] M. Zhang, L. Yuan, X. Wang, H. Fan, X. Wang, X. Wu, H. Wang, Y. Qian, J. Solid State Chem., **181**, 294 (2008). DOI: 10.1016/j.jssc.2007.12.011
[8] L. Xiao, Y. Su, X. Zhou, H. Chen, J. Tan, T. Hu, J. Yan, P. Peng, Appl. Phys. Lett., **101**, 041913 (2012). DOI: 10.1063/1.4733386
[9] X. Xu, H. Xiao, W. Guo, P. Gao, S.H. Peng, J. Inorg. Mater., **26**, 417 (2011). DOI: 10.3724/SP.J.1077.2011.00417
[10] D.J. Late, S. Karmakar, M.A. More, S.V. Bhoraskar, D.S. Joag, J. Nanopart. Res., **12**, 2393 (2010). DOI: 10.1007/s11051-009-9798-4
[11] S.A. Kamble, D.M. Phase, S. Ghorui, D. Bhattacharjee, S.V. Bhoraskar, V.L. Mathe, Physica B, **626**, 413289 (2022). DOI: 10.1016/j.physb.2021.413289
[12] S. Zhou, J. Zhang, D. Liu, Z. Lin, Q. Huang, L. Bao, R. Ma, Y. Wei, Acta Mater., **58**, 4978 (2010). DOI: 10.1016/j.actamat.2010.05.031
[13] A.A. Svinukhova, A.Y. Pak, P.V. Povalyaev, D.S. Nikitin, A. Nassyrbayev, Mater. Chem. Phys., **328**, 129973 (2024). DOI: 10.1016/j.matchemphys.2024.129973
[14] A.Ya. Pak, D.V. Rybkovskiy, Yu.Z. Vassilyeva, E.N. Kolobova, A.V. Filimonenko, A.G. Kvashnin, Inorg. Chem., **61**, 6773 (2022). DOI: 10.1021/acs.inorgchem.1c03880
[15] A.A. Gumovskaya, A.Ya. Pak, P.V. Povalyaev, *Sposob polucheniya poroshka diborida titana*, Patent RU 2805065 C1 (published on October 11, 2023) (in Russian).

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