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SYNTHESIS OF MANGANESE DIBORIDE BY MICROWAVE ASSISTED METHOD

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Nanosized powder of manganese diboride (MnB_2) was synthesized by the microwave heating method for the first time. A stoichiometric mixture of manganese dioxide (MnO_2) and magnesium dodecaboride (MgB_{12}) was used as raw material, where magnesium dodecaboride served as the reducing agent and a source of boron. A domestic microwave oven was used to generate microwave radiation. Phase composition of the initial mixture and the obtained product were examined by XRD studies, of the initial mixture and formation of a single-phase final product, MnB_2. Average particle size of synthesized manganese diboride (40 *nm*) was calculated on the basis of Scherer's formula.

Figs. 2, references 24.

Many of metal borides have been synthesized because of their excellent characteristics, such as high heat and wear resistance, high hardness, etc. For example, rhenium diboride (ReB_2) is among the hardest materials with metallic behavior [1], MgB_2 is a superconductor with T_c=39 *K* [2].

Manganese borides are considered as potential promising materials due to their several high physicochemical characteristics (hardness, wear and corrosion resistance, etc.) and incompressibility related to the high valence electron densities of the transition metals [3]. A large variety of manganese borides, such as Mn_4B, Mn_2B, MnB, Mn_3B_4, MnB_2, MnB_4, MnB_{12}, MnB_{23}, etc. are registered in the Mn-B system. Among these compounds manganese diboride (MnB_2) is considered as a perspective one due to its relatively high melting temperature, hardness and magnetism [4-7]. Aydin and Simsek [8] have predicted a superhard phase of MnB_2 with ReB_2-type structure, which is the ground state of MnB_2 at ambient conditions. However, to date only AlB_2-type (space group P6/mmm) MnB_2 has been successfully synthesized by arc melting [7].

There are many methods to synthesize metal borides. One of prominent methods is self-propagating high-temperature synthesis (SHS). Many transition

metal borides were synthesized by SHS [9]. Mechanical alloying and heat treatment were used to synthesize borides in the Cr-B and Mo-B systems [10] and arc melting technique for the Mn-B system [11].

It should be noted that existing methods allow to synthesize MnB_2 at very high temperatures, high pressures and long durations of the process [12].

In recent years, microwave (MW) radiation has been widely used for the synthesis of organic and inorganic compounds [13-15]. Microwave radiation is also used to synthesize carbides, borides, nitrides, halides of transition metals from precursors that included powdered metals and or metal oxides [16-21]. In these studies domestic microwave ovens with an operating frequency of 2.45 *GHz* and power up to 1-1.5 *kW* were mainly used as heaters. In most of these studies microwave preparations reported have been made on the laboratory scale of only a few grams.

In this study all experiments have been conducted using approximately the same quantities of initial powder mixtures by the use of a domestic microwave oven operating at 2.45 *GHz* and with a maximum output power of 900 *W*. Thus, for the first time microwave heating method was applied for the synthesis of manganese diboride, enabling to elaborate a fast and efficient approach for preparing nanocrystalline MnB_2.

Experimental

Manganese (IV) oxide, MnO_2 (analytical grade), magnesium dodecaboride, MgB_{12}, (analytical grade) were used as raw materials for preparation of Mn-B compounds. It is a matter of general experience that to apply microwave heating, it is necessary that the substance has a high value of the dielectric constant [22-23]. Among manganese oxides the used MnO_2 oxide exhibits the strongest MW absorption [24].

In experiments manganese (IV) oxide and magnesium dodecaboride powders have been weighed and carefully mixed in stoichiometric ratio in a quartz cup for two hours using a magnetic stirrer. After mixing, the initial mixture was placed into a quartz tube that was equipped with a pure nitrogen (99.9%) purging device and the mixture was kept under laminar flow at least two hours. The reaction mixture was subjected to microwave radiation for 10 min by a modified domestic microwave oven with power 900 *W* under constant flow of nitrogen (flow rate of 20 *ml*/*min*).

The stoichiometric ratio of the initial mixture was calculated taking into account that manganese (IV) oxide has to be reduced by magnesium and boron together, and the residual boron should be enough to form manganese diboride. The following overall reaction describes the mentioned conversions:

$$19MnO_2 + 5MgB_{12} = 19MnB_2 + 5MgO + 11B_2O_3 \quad (1)$$

After cooling, the obtained product was washed by 5% sodium hydroxide, then with 5% hydrochloric acid, cleaned with deionized water. These procedures ensure practically complete removing of undesirable compounds (MgO and B_2O_3) from the obtained end product. Then the remained residue was filtered and dried in an oven at 105 ± 0.5ºC and left for about 12 *hrs*.

Results and discussion

The washed and dried end product was characterized by XRD analysis using diffractometer DRON-3.0 (Burevestnik, Russia) with Cu Kα radiation. XRD pattern is shown in Fig.. Identification of XRD patterns by PCPDFWIN data (#350788) base shows peaks at 29.7°, 34.4°, 45.95°, 61.1°, 61.7°, 69.8° compatible with MnB_2 database degrees.

By the use of Empirean,PANalitycal, diffractometer with Cu Kα radiation XRD examination of the raw mixture has been also done (Fig. 2). From the obtained XRD patterns it is obvious that the initial mixture contains two compounds: MnO_2 and MgB_{12}. The comparison of the raw mixture and final product XRD patterns shows that there are no any coincidence of exist pattern. Based on comparison one can conclude that the raw materials are converted completely.

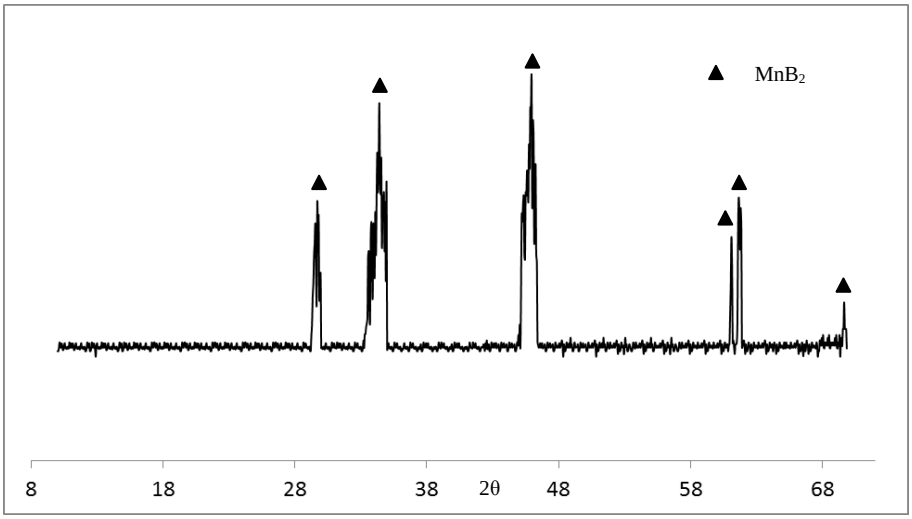

Fig. 1. XRD pattern of the washed pruduct.

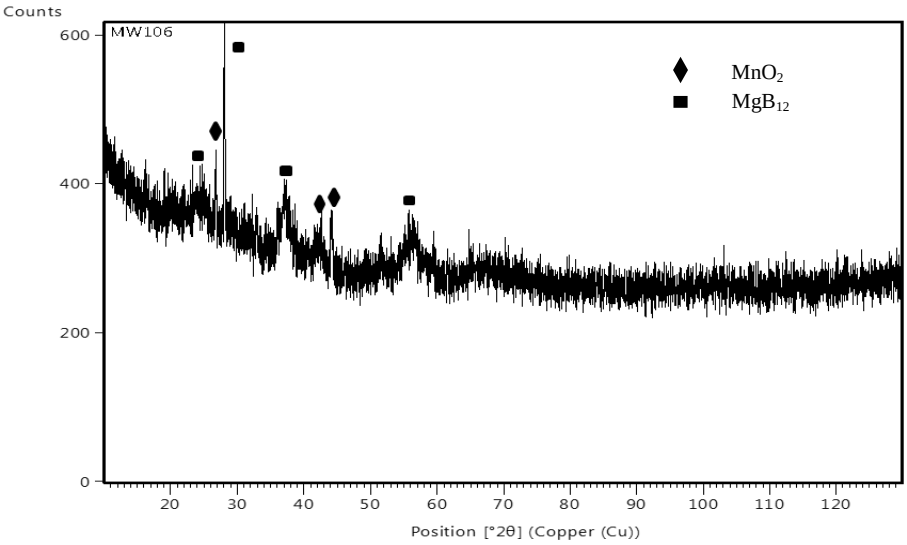

Fig. 2. XRD pattern of the raw mixture.

Particle size of manganese diboride (MnB_2) was calculated using Scherrer's formula:

$$d \cdot \frac{K \cdot \lambda}{\beta \cdot \cos\theta}, \qquad (2)$$

where d is the average size of particles, K is the shape factor (in this case K=0.9), λ is the X-ray wavelength, β is the line broadening at the half of maximum intensity, after subtracting the instrumental line broadening (in radians), θ is the Bragg angle (in degrees).

Based on XRD analysis results (Fig. 1) and using the known magnitudes for λ, β and θ the average particle size for the formed MnB_2 powders was calculated by equation (2) to be approximately 40 *nm*.

Conclusions

Nanopowders of MnB_2 were synthesized by the microwave heating method for the first time. The results of XRD examinations point to practically 100% conversion of the initial mixture. Average particle size of synthesized manganese diboride is 40 *nm*.

ՄԱՆԳԱՆԻ ԴԻԲՈՐԻԴԻ ՍԻՆԹԵԶԸ ՄԻԿՐՈԱԼԻՔԱՅԻՆ ԵՂԱՆԱԿՈՎ

Դ.Ն. ԴԱՎԹՅԱՆ

Առաջին անգամ միկրոալիքային վառարանային եղանակով սինթեզվել են մանգանի դիբորիդի (MnB2) նանոփոշիներ, օգտագործելով մանգանի երկօսիդի (MnO2) և մագնեզիումի դոդեկաբորիդի (MgB12) ստեխիոմետրիկ բաղադրությամբ ելային խարնուրդը: Մագնեզումի դոդեկաբորիդը կիրառվել է որպես վերականգնիչ և բորի աղբյուր: Իբրև միկրոալիքի աղբյուր կիրառվել է կենցաղային միկրոալիքային վառարանը: Միկրոալիքային սինթեզի տևողությունը կազմել է 10 րոպե: Ռենտգենաֆազային ուսումնասիրությունների հիման վրա ցույց է տվել, որ տեղի է ունենում ելանյութերի լրիվ փոխարկում: Սինթեզված մանգանի դիբորիդի նանոհատիկների միջին չափը գնահատվել է Շերերի հայտնի բանաձևով և կազմել է 40 նմ:

МИКРОВОЛНОВЫЙ СИНТЕЗ ДИБОРИДА МАРГАНЦА

Д. А. ДАВТЯН

Впервые методом микроволнового нагрева синтезированы нанопорошки диборида марганца (MnB_2). В качестве исходных веществ была использована стехиометрическая смесь диоксида марганца (MnO_2) и додекаборида магния (MgB_{12}). Последний служил как восстановитель и одновременно источник бора. Нагрев реагирующей смеси осуществлялся в бытовой микроволновой печи. Продолжительность микроволнового синтеза составляла 10 *мин*. Рентгенофазовым анализом установлено полное превращение исходных веществ. Средний размер частиц (40 *нм*) синтезированного диборида марганца оценен по известной формуле Шерера.

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