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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Solid-Phase Synthesis of Sodium-Bismuth Tungstate $NaBi(WO_4)_2$

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Abstract—Results of a solid-phase synthesis of polycrystalline sodium-bismuth tungstate $NaBi(WO_4)_2$ from $NaNO_3$, Na_2WO_4, Bi_2O_3, and WO_3 are presented. The optimal synthesis conditions are determined and a technological flow chart for synthesis of a single-phase product is suggested.

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Double tungstates attract attention as matrices for rare-earth lasers owing to the large absorption cross-section of a rare element in their lattice. Particular position among these compounds is occupied by the $NaBi(WO_4)_2$ crystal having high density, optical quality, and radiation hardness, which is of interest for quantum electronics, acousto-optics, and high-energy physics [1]. It has been found that this compound melts congruently, with no polymorphic transformations occurring below the melting point. Therefore, $NaBi(WO_4)_2$ single crystals can be grown by the Czochralski method. In crystallization from a congruent melt, the final result is strongly affected by deviations from stoichiometry, which commonly leads to variation of the melting point of the resulting crystal. The stoichiometry and homogeneity of the melt depend on the starting stock.

In [1], the melt was prepared from a stock produced by mechanical mixing of starting substances in a Na_2CO_3 : Bi_2O_3 : $4WO_3$ molar ratio. The melting point of the $NaBi(WO_4)_2$ crystals obtained was 920°C.

Volkov V. et al. [2] tested, using the same starting substances, three variants of stock preparation and came to a conclusion that the optimal way is to use the stock in the form of a polycrystalline $NaBi(WO_4)_2$. In this case, the melt can be more easily obtained in a cylindrical shape with a planar crystal–melt interface, with the melting points of the resulting crystals equal to 935°C. Polycrystalline $NaBi(WO_4)_2$ was synthesized in two stages by the reactions:

$$Na_2CO_3 + 4WO_3 = Na_2W_4O_{13} + CO_2\uparrow, \quad (1)$$

$$Na_2W_4O_{13} + Bi_2O_3 = 2NaBi(WO_4)_2. \quad (2)$$

To obtain the intermediate $Na_2W_4O_{13}$ by reaction (1), a stoichiometric mixture of the starting components was pelletized and annealed at a temperature of 760°C for 70–100 h. In the second stage, this intermediate was mixed with Bi_2O_3, pelletized, and annealed at 860°C for 100 h.

Hence follows that the synthesis of polycrystalline $NaBi(WO_4)_2$ by this method is time- and energy-inefficient because of the low rates of solid-phase reactions (1) and (2).

The aim of this study was to intensify the solid-phase synthesis of $NaBi(WO_4)_2$.

EXPERIMENTAL

To raise the rate of solid-phase reactions, we studied the synthesis of $NaBi(WO_4)_2$, with $NaNO_3$ and Na_2WO_4 used as starting sodium-containing compounds. Stoichiometric mixtures of the starting components were prepared in a TEFAL household blender, without subsequent pelletization. The mixtures were calcined in alundum crucibles in a muffle furnace at a heating rate of 15 deg min^{-1} to a temperature of 850°C in the course of 8 h.

The phase composition of the powders was determined

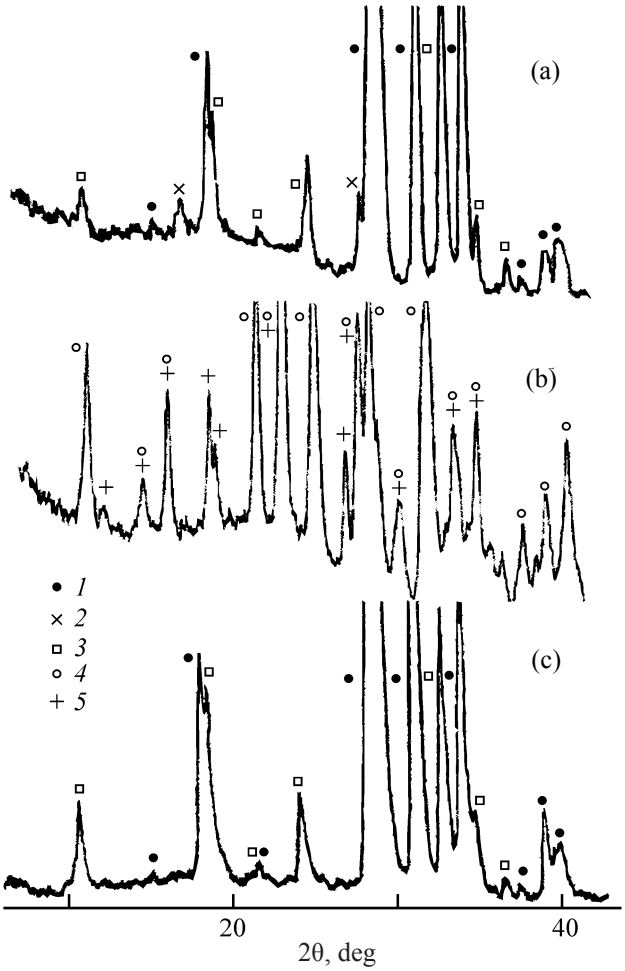


Fig. 1. X-ray diffraction patterns of the products of reactions (a) (3), (b) (4), and (c) $Na_2W_4O_{13} + Bi_2O_3$. (2θ) Bragg angle; the same for Fig. 2. (*1*) $NaBi(WO_4)_2$, (*2*) Bi_2O_3, (*3*) $Na_5Bi(WO_4)_4$, (*4*) $Na_2W_4O_{13}$, (*5*) $Na_2W_2O_7$.

by X-ray phase analysis (XPA) on a DRON-2 diffractometer with $Cu_{K\alpha}$ radiation and a graphite monochromator and the counter moving at a rate of 2 deg min_{-1}. The phase identification was performed using the JCPDS database. A differential-thermal analysis (DTA) of the samples was made with a NETZSCH STA 409 PC/PG synchronous thermal analyzer in the temperature range 25–1100°C at a heating rate of 10 deg min^{-1} in a corundum crucible in the atmosphere of argon.

With $NaNO_3$ used, the synthesis was carried out in a single or two stages. The single-stage synthesis by the reaction

$$Na_2NO_3 + Bi_2O_3 + 4WO_3 =$$

$$2NaBi(WO_4)_2 + O_2\uparrow + NO\uparrow + NO_2\uparrow \quad (3)$$

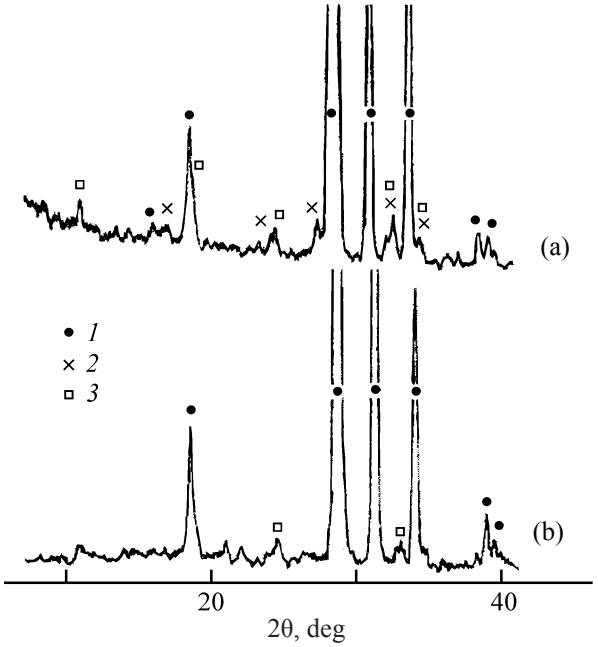


Fig. 2. X-ray diffraction patterns of the products of reactions (a) (5) and (b) (6). (*1*) $NaBi(WO_4)_2$, (*2*) Bi_2O_3, and (*3*) $Na_5Bi(WO_4)_4$.

demonstrated (Fig. 1a) that the final product contains admixtures of $Na_5Bi(WO_4)_4$ and Bi_2O_3 compounds.

In the two-stage synthesis, the first stage yielded the intermediate $Na_2W_4O_{13}$ by the reaction

$$2Na_2NO_3 + 4WO_3 = 2Na_2W_4O_{13} + O_2\uparrow + NO\uparrow + NO_2\uparrow \quad (4)$$

It was found that isothermal keeping at 500°C for 2 h provides formation of almost pure $Na_2W_4O_{13}$: the X-ray diffraction pattern in Fig. 1b contains, together with strong reflections from the main substance, several weak reflections from $Na_2W_2O_7$. The second stage was performed by reaction (2). The synthesis product was a well sintered monolith. The possible reason is that $Na_2W_4O_{13}$ and Bi_2O_3 melt at 780 and 820°C, respectively, i.e., a truly solid-phase reaction occurs in this case at 780°C, with a liquid phase appearing at higher temperatures and promoting the sintering of the final product. The X-ray diffraction pattern of the resulting product (Fig. 1c) contains, in addition to strong reflections of $NaBi(WO_4)_2$, comparatively strong reflections from the compound $Na_5Bi(WO_4)_4$ and a residual oxide Bi_2O_3. The intensities of these reflections in the X-ray diffraction patterns in Figs. 1a and 1c are almost equal. This led to a conclusion

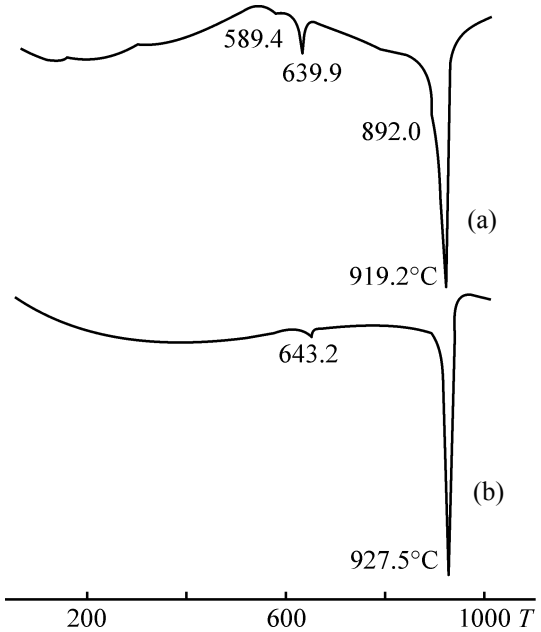


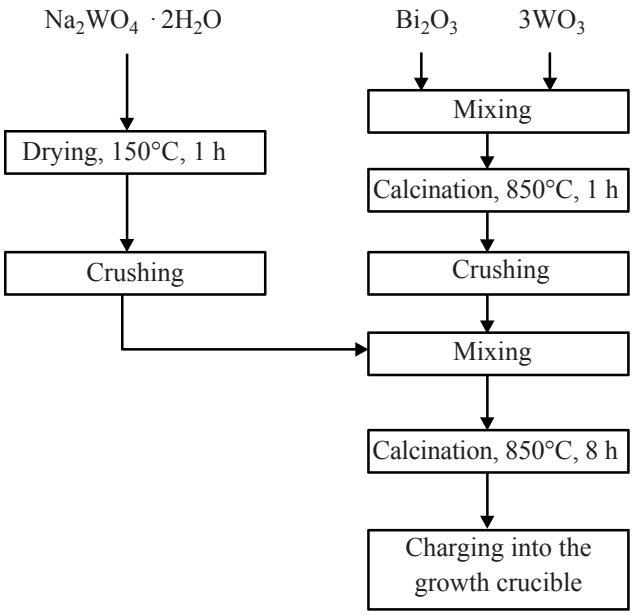
Fig. 3. DTA curves of the products of reactions (a) (5), (b) (6). (*T*) Temperature, °C.

that the synthesis variants considered above fail to yield single-phase $NaBi(WO_4)_2$.

With Na_2WO_4 used, a single-stage synthesis by the reaction

$$Na_2WO_4 + Bi_2O_3 + 3WO_3 = 2NaBi(WO_4)_2 \quad (5)$$

Technological flow chart for synthesis of polycrystalline $NaBi(WO_4)_2$



demonstrated that a more single-phase $NaBi(WO_4)_2$ is obtained in this way; however, strong reflections of $Na_5Bi(WO_4)_4$ and Bi_2O_3 are present in the X-ray diffraction pattern in Fig. 2a. The DTA curve of this product (Fig. 3a) shows four endothermic effects. These effects are identified as follows: that at 589.4°C corresponds to a polymorphic transformation of the remaining Na_2WO_4; those at 639.9 and 898°C, to melting of intermediate products; and that at 919.2°C, to melting of the final product. Hence follows that in this case, too, the final product strongly differs from the single-phase $NaBi(WO_4)_2$.

The results of all the synthesis variants demonstrated that the obstacle to synthesis of the single-phase $NaBi(WO_4)_2$ is the incomplete reaction of Bi_2O_3 with WO_3 and $Na_2W_4O_{13}$. A possible way out is preliminary binding of Bi_2O_3 with WO_3. For this purpose, a $Bi_2O_3 + 3WO_3$ mixture was calcined at 850°C for 1 h. An X-ray phase analysis of the thus obtained cake demonstrated that it is composed of a mixture of Bi_2WO_6, $Bi_2W_2O_9$, and WO_3. The cake was crushed and used to synthesize $NaBi(WO_4)_2$ by the reaction

$$Na_2WO_4 + (0.5Bi_2WO_6 + 0.5Bi_2W_2O_9 + 1.5WO_3) = 2NaBi(WO_4)_2. \quad (6)$$

An X-ray phase analysis of the product (Fig. 2b) demonstrated that it is an almost single-phase $NaBi(WO_4)_2$. The DTA curve of this product (Fig. 3b) shows onlyasingle additional weak endothermic effect at 643.2°C. The product is obtained in the form of a cake with a density of 6.2g cm^{-3}, which constitutes 81.9% of the X-ray density of $NaBi(WO_4)_2$. The comparatively high density of the product allows a single introduction of the starting substance into the growth crucible in growth of $NaBi(WO_4)_2$ single crystals by the Czochralski method.

The results of the study are generalized in the form of a technological flow chart. It envisages synthesis of polycrystalline $NaBi(WO_4)_2$, with Na_2WO_4, Bi_2O_3, and WO_3 as starting substances, in two stages: (1) calcination of a $Bi_2O_3 : 2WO_3$ mixture at 850°C for 1 h and (2) calcination of a mixture of a crushed cake and a stoichiometric amount of Na_2WO_4 at 850°C for 8 h. Compared with the known technique for synthesis of $NaBi(WO_4)_2$, the method we developed makes it possible to shorten the time of sintering of the starting substances from 170–200 h to 9 h, drop the technological procedure of compaction of the starting substances,

and to raise the density of the sintered product from 5.1 to 6.2 g cm^{-3}.

CONCLUSIONS

(1) A study aimed to intensify the solid-phase synthesis of polycrystalline $NaBi(WO_4)_2$ at 850°C in the course of 8 h was carried out. It was shown that, with $NaNO_3$, Bi_2O_3, and WO_3 used as starting substances, synthesis in a single or two stages fails to provide a single-phase product.

(2) Almost single-phase polycrystalline $NaBi(WO_4)_2$ is formed when Na_2WO_4, Bi_2O_3, and WO_3 are used as starting substances, provided that Bi_2O_3 is preliminarily bound with WO_3 by calcination of their stoichiometric mixture at 850°C for 1 h.

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