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LETTER TO THE EDITOR

Borophosphates: Hydrothermal and Microwave-Assisted Synthesis of $Na_5[B_2P_3O_{13}]$

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$Na_5[B_2P_3O_{13}]$ was first prepared by high temperature synthesis ($T_{max} = 780$°C) and was characterized by X-ray single crystal investigations recently. We have now succeeded in the hydrothermal synthesis of the compound and obtained single-phase products at 150°C after 1–2 days. A microwave-assisted synthesis takes only 2 min to transform a solid mixture of borate and phosphate hydrates into the crystalline title compound. Pure $Na_5[B_2P_3O_{13}]$ melts at 747°C and solidifies during cooling by formation of a homogeneous glass. © 1998 Academic Press

$Na_5[B_2P_3O_{13}]$ was first prepared from mixtures of $NaH_2PO_4 \cdot 2H_2O$ and $NaBO_2 \cdot 4H_2O$ by high temperature synthesis in platinium crucibles ($T_{max} = 780$°C); the crystal structure (Fig. 1) contains BO_4- and PO_4 tetrahedra which share common vertices to form infinite chain anions ${}^1_\infty[B_2P_3O_{13}]^{5-}$ running along the [100] direction of the monoclinic crystal structure (1). Up to now, a respectable number of borophosphates (intermediate phases in the systems $M_2O/MO\text{-}B_2O_3\text{-}P_2O_5(\text{-}H_2O)$) have already been known and a first approach to borophosphate structural chemistry has been developed only recently (2). Most of the borophosphates are preferably prepared by the hydrothermal method at temperatures below 200°C (2). We therefore followed this line in order to prepare the title compound under hydrothermal conditions and at the same time we extended our investigations (3) to a microwave-assisted variant (4). The basic idea for a microwave-assisted preparation of borophosphates is consistent with the observation of high microwave susceptibilities of those phosphate and borate hydrates (5), which are used as educt materials.

Pure $Na_5[B_2P_3O_{13}]$ is obtained by hydrothermal synthesis starting from mixtures (12 g) of $NaBO_2 \cdot 4H_2O$ (purum, Fluka) and $NaH_2PO_4 \cdot 2H_2O$ (purum, Merck) in a 2 : 3 molar ratio. After addition of 15 ml H_2O the system was heated up to 90°C and the total volume was reduced to 10 ml by evaporation of water; the highly viscous solution was filled into Teflon autoclaves (Roth, degree of fill 50%) and treated at 150°C for two days. The crystalline reaction product ($Na_5[B_2P_3O_{13}]$, monoclinic prisms (Fig. 2) up to 0.4 mm in length) was separated from the solution by filtration and finally washed with water. The reaction can also be carried out by using the peroxoborate $NaBO_3 \cdot 4H_2O$ as a borate source.

For microwave-assisted synthesis of $Na_5[B_2P_3O_{13}]$ a dry and ground solid mixture (2 g) of $NaBO_2 \cdot 4H_2O$ and $NaH_2PO_4 \cdot 2H_2O$ (molar ratio of 2: 3) was filled into a Teflon autoclave and was treated in a conventional kitchen microwave system (2.450 GHz; max 1650 W) for the short period of only 2 min. After this extremly short time of reaction the solid product was already identified by X-ray

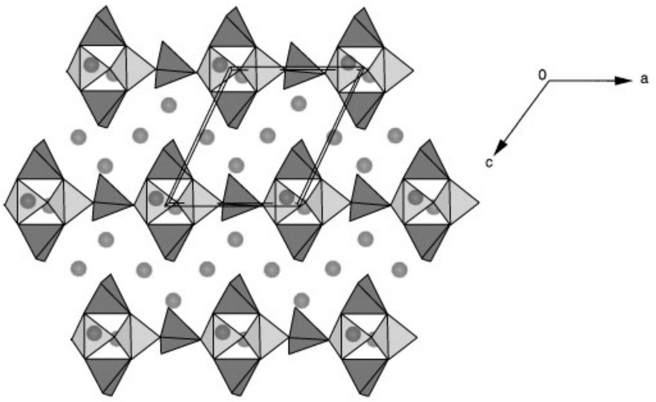

FIG. 1. Crystal structure of $Na_5[B_2P_3O_{13}]$ (monoclinic, $P2_1$, $a = 671.1(9)$ pm, $b = 1161.8(12)$ pm, $c = 768.6(9)$ pm, $\beta = 115.2(1)°$, $Z = 2$), view along [010]; dark: PO_4-tetrahedra, light: BO_4-tetrahedra; spheres: Na^+ [1].

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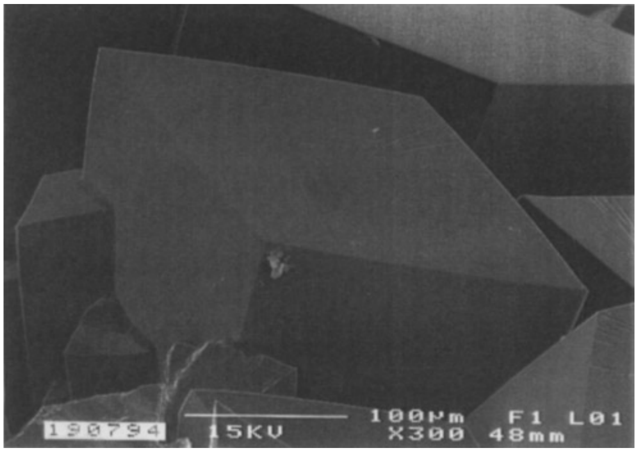

FIG. 2. SEM photograph of a single crystal of $Na_5[B_2P_3O_{13}]$, obtained by hydrothermal synthesis at 150°C.

powder investigations (STOE, STADI P2) as single-phase $Na_5[B_2P_3O_{13}]$ (Fig. 3). The crystallinity of the reaction product is improved by additional annealing at 100°C for two hours. The basic reaction for the microwave-assisted synthesis can be represented by

$$2NaBO_2 \cdot 4H_2O + 3NaH_2PO_4 \cdot 2H_2O \rightarrow Na_5[B_2P_3O_{13}] + 9H_2O.$$

The first step (~50 s) of the reaction is the loss of water molecules from the phosphate component; even the dehydrated product is still active with respect to microwave absorbtion (5). Dehydration of the borate component takes place simultaneously (5). Based on the earlier observations (5), the estimated maximum temperature of the system after 2 min treatment with microwave radiation is expected not to exceed 200°C.

The thermal stability of pure $Na_5[B_2P_3O_{13}]$ was investigated by DTA (Netzsch STA 409 EP; Pt–Pt/Rh thermocouple; kaoline reference; corundum crucible; heating rate 5°C/min) : The borophosphate melts at 747°C (onset) and solidifies during cooling by formation of a homogeneous glass.

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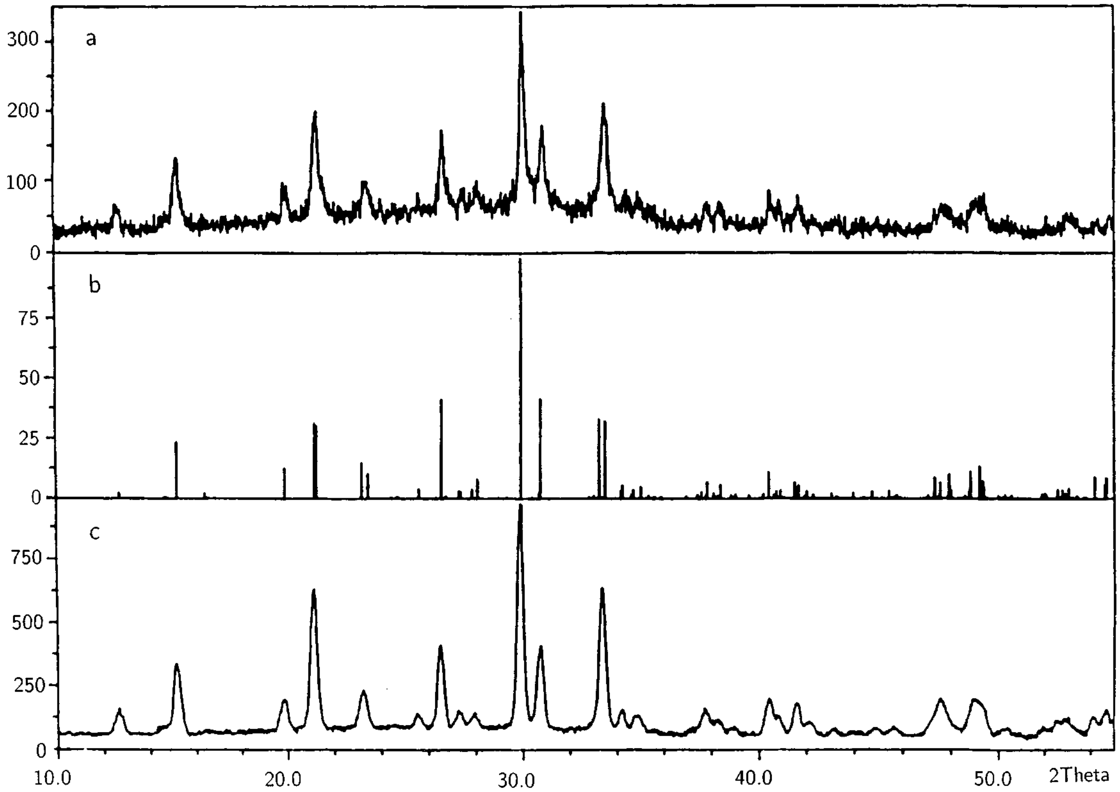

FIG. 3. X-ray powder patterns of $Na_5[B_2P_3O_{13}]$, obtained by microwave-assisted synthesis; (a) X-ray powder pattern after treatment with microwaves for 2 min; (b) X-ray powder pattern of $Na_5[B_2P_3O_{13}]$ calculated from crystal structure data (1); (c) X-ray powder pattern of a sample after 2 min of microwave treatment and additional annealing for 2 h at 100°C; Cu$K\alpha_1$-radiation.

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