Functional Materials 14, No.2 (2007)

Synthesis of strontium tetraborate SrB_4O_7 for single crystal growth

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Received March 2, 2007

The possibility of the single phase SrB_4O_7 synthesis through the amorphous phase formation stage has been shown. Using XPA and DTA methods, the formation of strontium borate hydrates has been determined to occur at $T = 95\pm5$°C in the course of strontium carbonate interaction with boric acid. The dehydration of strontium borate crystal hydrates results in amorphous phase formation. A further phase transition (borate rearrangement) of this phase at $T = 750$°C results in formation of polycrystalline SrB_4O_7.

Показана возможность синтеза монофазного SrB_4O_7 через стадию образования аморфной фазы. Методами ДТА и РФА установлено, что образование кристаллогидратов боратов стронция происходит при $T = 95\pm5$°C в процессе твердофазного взаимодействия ортоборной кислоты с карбонатом стронция. Обезвоживание кристаллогидратов боратов стронция приводит к образованию аморфной фазы, которая претерпевает фазовый переход (боратную перегруппировку) при температуре $T = 750$°C с образованием поликристаллического SrB_4O_7.

Nowadays, the strontium tetraborate SrB_4O_7 (SBO) crystals are under active investigation as polyfunctional materials. SBO belongs to the rhombic system, the $Pnm2_1$ space group, and has the following parameters: $a = 4.4255(7)$ Å, $b = 10.709(2)$ Å, $c = 4.2341(9)$ Å, $V = 200.7$ Å^3, $Z = 2$, $d_{calc} = 4.011$ g/cm^3, $Z = 2$. The SBO crystals are transparent in a wide spectral range (from 125 to 3200 nm) [1], and have high effective nonlinear optical coefficients comparable to those of $KTiOPO_4$ crystals [2, 3]. The high isomorphic capacity for lanthanide ions incorporation, high thermallystimulated luminescence yield combined with non-hygroscopicity allows one to consider SBO as a prospective material for the solid state dosimetry [4–6]. Activated SBO single crystals find practical applications as high pressure sensors or magneto-optical materials [7, 8].

At present, the synthesis of polycrystalline strontium tetraborate [9, 10] and SBO single crystals growing technology [1, 11] are well studied. However, there is a problem with a reproducible synthesis of the compound due to possible competitive formation of various strontium borate phases. The presence of impurity phases results in a significant degradation of functional characteristics of SBO based storage phosphors [10]. At the same time, the phase composition requirements for the SBO as the initial material for single crystal growth are much higher. According to the $SrO–B_2O_3$ phase diagram [12], the SrB_4O_7 compound is characterized by a narrow homogeneity range. Moreover, a compound $Sr_4B_{14}O_{25}$ ($4SrO{\cdot}7B_2O_3$) has been found in a later work [13], very similar in chemical composition to SBO ($SrO{\cdot}2B_2O_3$). The stoichiometry distortion of the SBO charge more than by 2 mol. % boron oxide will result in changed melt composition that can cause the growth process breakdown due to deviation of the melt composition from the SBO crystallization concentration range on the phase diagram. The traditional use of

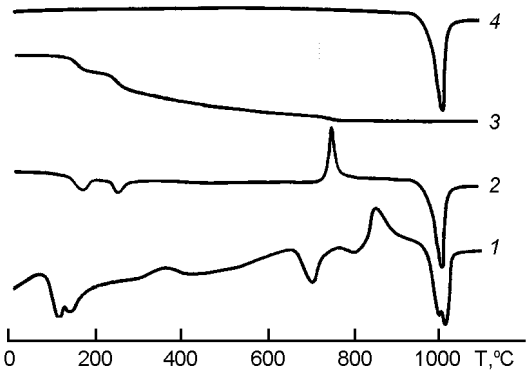

Fig. 1. DTA curves of the SrB_4O_7 samples: *1*, raw stoichiometric mixture of powders; *2*, after calcination at $T = 95$°C (10 h); *3*, DTG curve corresponding to the DTA curve *2*; *4*, after calcination at $T = 95$°C (10 h) and $T = 890$°C (10 h).

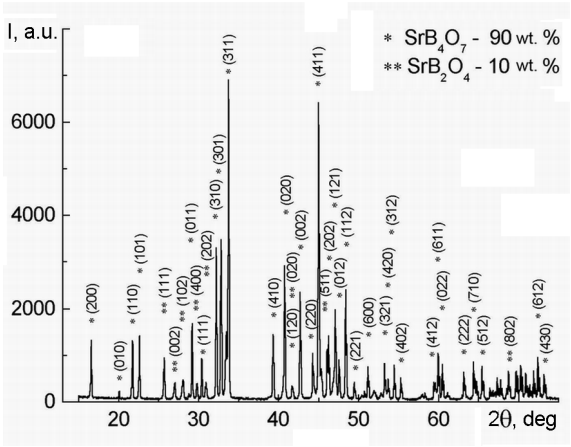

Fig. 2. X-ray diffraction spectrum of SrB_4O_7 sample after calcination at $T = 900$°C (10 h).

boron oxide excess provides only partial solution of this problem because of the high melt viscosity and long duration of the growth cycle.

Usually, the charge for borate single crystal growth is synthesized using the solid state method. The indium borate $InBO_3$ is known can be obtained by borate rearrangement [14]. According to [15], strontium borates can be synthesized by dehydration of corresponding hydrates (through intermediate amorphous phases). However, the possibility of SBO obtaining through amorphous phases is scarcely described in literature. Thus, this work is aimed at study of the SBO formation process in the $SrO–B_2O_3$ system.

SrB_4O_7 was synthesized in an air in a platinum crucible. The samples were heat treated in a KO-14 muffle furnace. The special purity grade strontium carbonate $SrCO_3$ and chemical purity grade boric acid H_3BO_4 were used as the starting materials for the SBO synthesis. Differential thermal analysis (DTA) was carried out using a Q-1500D (MOM) derivatograph in the dynamic mode at the heating rate of 5°C/min, using $\alpha–Al_2O_3$ powder as a reference. The X-ray phase analysis (XPA) of samples was performed on a Siemens D500 powder diffractometer (CuK_α-radiation).

First, let the processes taking place during SBO solid state synthesis be considered. The DTA has shown (Fig. 1, curve *1*) that, after decomposition of boric acid ($T = 120–140$°C) and strontium carbonate ($T = 660–700$°C), the solid state reaction of the components occurs at relatively high temperatures of 850–900°C. Since the solid state interaction is limited by diffusion, a prolonged annealing at pre-melting temperatures is necessary. This results in the boron oxide volatilization and the compound stoichiometry distortion.

The XPA pattern of the sample heat treated at $T = 900$°C contains reflexes from several phases. In addition to the main crystalline phase of strontium tetraborate (90 wt. %), the strontium metaborate phase SrB_2O_4 (10 wt. %) depleted of boron has been revealed (Fig. 2). In accordance to the $SrO–B_2O_3$ phase diagram [13], the 90 % content of the main phase in the synthesized sample is insufficient for its usage as the initial charge for single crystal growth.

The next task was to establish the ways to strontium tetraborate synthesis by dehydration of its hydrate. Taking into account the boric acid feature to displace volatile acids from their salts [16], it is possible to obtain various borate hydrates by decomposition of strontium carbonate with boric acid. For this reason, the following reaction of strontium tetraborate hydrate formation has been proposed:

$$SrCO_3 + 4H_3O_3 \rightarrow$$
$$\rightarrow SrB_4O_7 \cdot nH_2O + CO_2 + (6 - n) \cdot H_2O.$$

To synthesize $SrB_4O_7 \cdot nH_2O$, the strontium carbonate $SrCO_3$ and boric acid H_3BO_3 in stoichiometric ratio were thoroughly mixed and ground to increase the mixture reactivity. Then the obtained sample was placed in the platinum crucible and calcined at 90–95°C for at least 10 h. The completeness of the reaction was con-

trolled by XPA and DTA. According to the XPA data, the $SrB_6O_{10}{\cdot}4H_2O$, $Sr(B(OH)_4)_2$, $Sr_2(B_2O_8(OH)_2B(OH)_3(H_2O)$ and $Sr(B_8O_{11}(OH)_4)$ phases were found after the sample heat treatment ($T = 90$–95°C, $t = 10$ h). The total stoichiometry corresponded to the $SrB_4O_7{\cdot}nH_2O$ composition. The presence of several phases in the mixture may be caused by the solid state synthesis utilization instead of precipitation from aqueous solution [17]. Thus, strontium tetraborate obviously does not form hydrates, in contrast to other strontium borates [17, 18].

In the DTA curve of the sample obtained according to reaction, endothermic peaks with maxima at 170°C and 250°C accompanied by simultaneous mass loss were observed (Fig. 1, curves *2*, *3*). This indicates the stepwise dehydration of strontium borate hydrates resulting in an amorphous phase formation. The amorphous phase presence has been confirmed by XPA: a characteristic halo in the small-angle region has been observed in the X-ray diffraction pattern of the sample. The calculated mass loss from the sample corresponded to the removal of two water molecules. The further mass loss occurred probably due to the removal of $(OH)^-$ groups from the compounds forming the mixture. This loss is observed till $T = 750$°C. The total mass of the crystallized sample corresponded to theoretical mass of the pure SrB_4O_7. The peaks of thermal effects corresponding to $SrCO_3$ decomposition and interaction of strontium carbonate with boron oxide (usually observed at $T = 660$–900°C (Fig. 1, curve *1*) when the solid state reaction is used [5]), were absent in the experimental heating curve.

Temperature increase up to $T = 750$°C results in appearance of an exothermic peak in the DTA curve corresponding to the amorphous phase crystallization (Fig. 1, curve *2*). This is a characteristic effect for numerous synthetic borates [19] and is refereed to as borate rearrangement [20]. At the dehydration, the borate crystal lattice disintegrates and material transfers to amorphous state. A further heating causes crystallization of the amorphous phase accompanied by exothermal effect that can be seen in the DTA curve. Generally, the DTA data shown in the Fig. 1, curve *2*, are typical of the borate rearrangement process.

Accordingly to the XPA data, the content of the crystalline SrB_4O_7 phase in the sample calcined at $T = 750$°C during 6 h was 66 wt. %. The SrB_2O_4 and SrB_6O_{10} compounds were revealed as impurity phases. This evidences the incomplete reaction or the competition in formation of several strontium borates in the 700–850°C temperature range [18] (as well as in the case of solid state reaction).

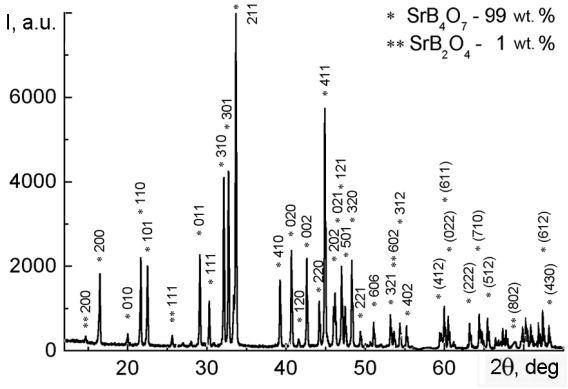

Fig. 3. X-ray diffraction spectrum of SrB_4O_7 sample after calcination at $T = 95$°C (10 h) and $T = 890$°C (10 h).

To obtain a single-phase compound, the intermediate grinding stage has been used (to increase the activity of reagents) and the sample has been additionally annealed at $T = 890$°C during 24 h. After such heat treatment, the single-phase SBO has been synthesized (within the experimental error of the XPA, Fig. 3). The obtained DTA curve for SBO (Fig. 1, curve *3*) contains only one endothermic peak at 1015°C corresponding to the congruent melting of the compound [13]. The polycrystalline SBO synthesized by the technique described above has been used successfully to grow SBO single crystals [21]. Thus, the borate rearrangement method can be used to obtain the single-phase SBO that is applicable for single crystal growth.

To conclude, the peculiarities of SBO phase formation in the SrO–B_2O_3 system have been studied using differential thermal and X-ray phase analysis. It has been determined that single-phase SrB_4O_7 appropriate for the single crystal growth can be synthesized by the following scheme: raw mixture of powders → strontium borate hydrates → amorphous phase → polycrystalline SrB_4O_7.

Acknowledgment. Authors thank Dr.V.N.Baumer and Dr.V.F.Tkachenko for XPA studies of the experimental samples.

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Синтез тетраборату стронцію SrB_4O_7 для вирощування монокристалів

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Показано можливість синтезу монофазного SrB_4O_7 через стадію утворення аморфної фази. Методами ДТА й РФА встановлено, що утворення кристалогідратів боратів стронцію відбувається при $T = 95\pm5$°C у процесі твердофазної взаємодії ортоборної кислоти з карбонатом стронцію. Зневоднювання кристалогідратів боратів стронцію приводить до утворення аморфної фази, в якій відбувається фазовий перехід (боратне перегрупування) при температурі $T = 750$°C з утворенням полікристалічного SrB_4O_7.