

## HYDROTHERMAL SYNTHESIS AND MORPHOLOGY OF EULYTITE-LIKE SINGLE CRYSTALS

D. E. Kozhbakhteeva, N. I. Leonyuk\*

Moscow State University, Geological Faculty, Moscow 119992/GSP-2, Russia

Visually homogeneous eulytite-type crystals  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  (BSO) and  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) have been synthesized by spontaneous nucleation in hydrothermal  $\text{NH}_4\text{F}$ ,  $\text{HClO}_4$  and  $\text{KOH}$  solutions. These crystals have also been obtained on the seeds of Czochralski grown bismuth germanate. Their growth rate increases with increasing concentration of solvent, crystallization temperature and temperature gradient. The synthetic crystals tend to grow with strongly developed  $\{211\}$  and  $\{2\bar{1}1\}$  faces. External and internal morphology of these crystals are similar to their natural prototype, and they can serve for identification of the simple forms in this mineral.

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### 1. Introduction

Since the seventies of the last century, eulytite-like structure have received much attention as polyfunctional materials with very attractive physical characteristics. They play an essential role in nuclear medicine, gamma-ray spectroscopy, high energy, oil well logging and in other applications relating to strong piezoelectric and acoustic, optically active and also photo-conductive in the visible range media as well as a medium-gain laser host for rare earth elements (for example, see refs. [1-4]). Among them, bismuth germanate  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) has many valuable properties such as activity in a short radiation wavelength, a light output as large as 10% of  $\text{NaI:Tl}$  and  $\text{CsI:Tl}$ , etc. On the other hand, bismuth silicate  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  (BSO) is more suitable for radiation detector applications in nuclear and high energy physics experiments because of its larger absorption and faster decay characteristics.

Large BGO and BSO single crystals have been grown by Czochralski method [1,4], but BSO has been also obtained using vertical Bridgman technique [5]. In these methods, however, very high purity of the initial mixture is needed, in order to obtain orthosilicates and orthogermanates with a good stoichiometry. Moreover, the crystals grown at high temperature crack easily. Another problem concerns the high commercial cost of germanium chemicals. For these reasons, this paper deals with hydrothermal growth of BSO and BGO crystals at moderate temperature conditions.

### 2. Experimental

The hydrothermal synthesis was carried out in 250-300 ml steel reaction vessels by the method of direct temperature gradient (from 60 ° to 100 °C) using  $\text{NH}_4\text{F}$ ,  $\text{HClO}_4$  and  $\text{KOH}$  mineralizers. Since these solutions strongly attack ferrous alloys, all autoclaves were lined with fluoroplastic, when temperature does not exceed 310 °C. The inserts were separated by perforated fluoroplastic diaphragms (5-10% of cross section) into two areas, dissolution and crystallization zones. The temperature was measured in both zones by two external thermocouples with accuracy of

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\* Corresponding author: leon@geol.msu.ru

$\pm 2$  °C. The pressure was kept at the level depending on the factor of filling up the autoclave. After experiments, solid phases were carefully washed and dried.

Spontaneously-nucleated BSO crystals were obtained from 7-8 wt.% KOH based hydrothermal solutions following earlier results for hydrothermal synthesis of  $\text{Bi}_{12}\text{SiO}_{20}$  crystals in the system  $\text{Bi}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-H}_2\text{O}$  [6]. The 10 wt.%  $\text{NH}_4\text{F}$  solution was used for BGO spontaneous crystallization. These solutions were previously saturated by dissolving the near stoichiometric  $\text{Bi}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{GeO}_2$  oxides with 3N and 4N purity at 450 °C and 310 °C for BSO and BGO respectively. By adding some amount of  $\text{Bi}_2\text{O}_5$  (for BSO) and  $\text{HNO}_3$  (in the case of BGO) to initial mixture, one suppressed reduction of  $\text{Bi}^{+3}$  in  $\text{Bi}_2\text{O}_3$  to metallic state. The level of pressure was at  $P = 20\text{-}50$  Mpa and the super saturation, created by forming a temperature difference between the zones of dissolution and spontaneous crystallization, was kept at a suitable level by decreasing temperature in the crystal growth zone during each of five- to ten-days experiments.

In the case of BSO and BGO crystal growth on seeds,  $\text{HClO}_4$  was used as a mineralizer. The starting material was prepared of spontaneously grown BGO, but BSO was sintered by solid state reactions at temperature of 910 °C during 20 hours. This mixture was loaded at bottom of the lining autoclave (dissolution area). The plate-like seeds were cut of BGO crystals grown by Czochralski method and fixed in the upper section (crystallization zone). Saturated solutions were transferred from the lower, and most heated, area into the higher one (more cold) owing to the thermal convection. As a result of supersaturating solution in the top of autoclave, an excess of dissolved BSO and BGO deposited on the seeds. Experimental conditions were as follows: temperature was 310 °C in the dissolution zone,  $\Delta T = 65$  °C,  $P = 30$  Mpa and experiment duration was 20 days.

The grown crystals were studied by chemical, spectral and electron microprobe analysis as well as by using optical and electron microscopy. Crystallographic indexes of simple crystal forms were calculated from data measured by means of optical goniometry and electron microscopy. Absorption spectra were measured by means SPECORD –M 40 spectrometer.

### 3. Results and discussion

Aggregates of BSO crystals up to 2-3 mm were obtained in all runs of BSO spontaneous growth (Fig. 1). Beside of this Si-rich silicate, another Bi-rich phase,  $\text{Bi}_{12}\text{SiO}_{20}$ , is stable.

Transparent and colorless BGO crystals with sizes up to 5 mm have also been synthesized by spontaneous nucleation (Fig. 2). No visible defects are in these cubic crystals, but the grown up material has isometric cracks (Fig. 2). There is the following correlation between the growth rate of different faces of the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals:  $V_{\{211\}} < V_{\{\bar{2}\bar{1}\bar{1}\}} < V_{\{310\}} < V_{\{110\}}$ . In both cases, BGO and BSO crystal growth, elevated concentrations of halogenide solutions promote other phases, like  $\text{BiOF}$  and/or  $\text{BiOCl}$ , to crystallize.

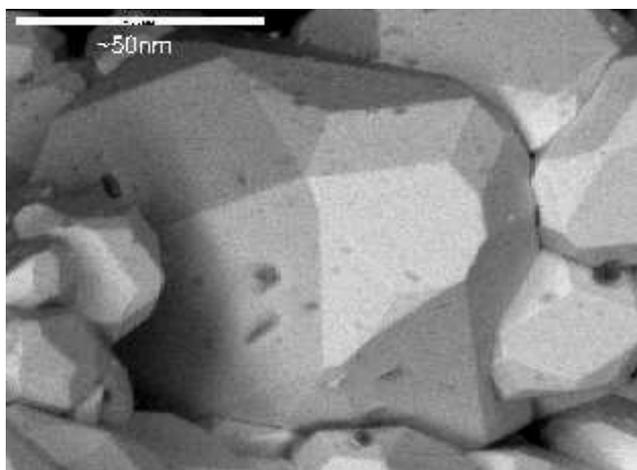


Fig. 1. Aggregated BSO crystals.

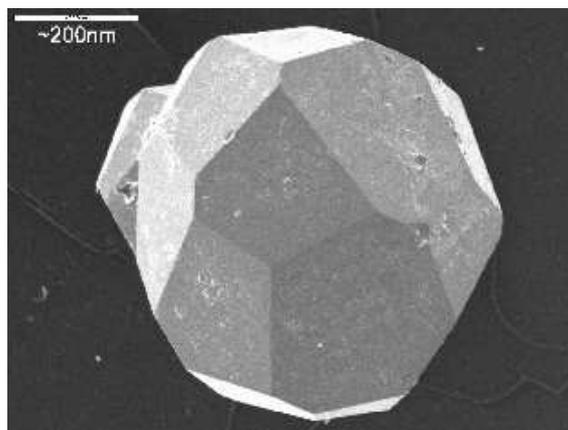


Fig. 2. BGO crystal grown by spontaneous nucleation.

Visually homogeneous and transparent BSO layers up to 0.5 mm as well as BGO layers up to 10 mm have also been obtained from halogenide hydrothermal solutions using the [111], [110] and [100] oriented BGO bars as seeds (Fig.3). Their growth rate increases with increasing concentration of solvent, crystallization temperature and temperature gradient.

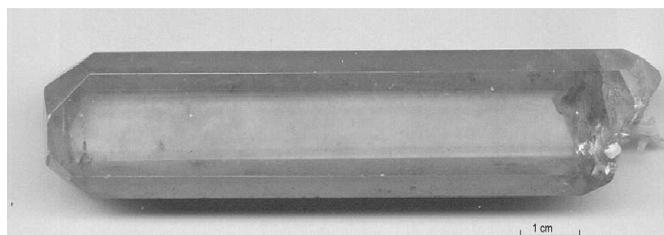


Fig. 3. BGO crystal grown on [111] oriented BGO bars-like seed.

The synthetic eulytite-type BSO and BGO crystals tend to grow with strongly developed and {11-2} faces. The secondary role play {102} and {110} simple forms. There are vicinal pyramids on {112} faces (Fig. 4). BGO crystals grown on the {111} oriented seeds are six-surfaced bars faceted by the simple form {112} at both tips.

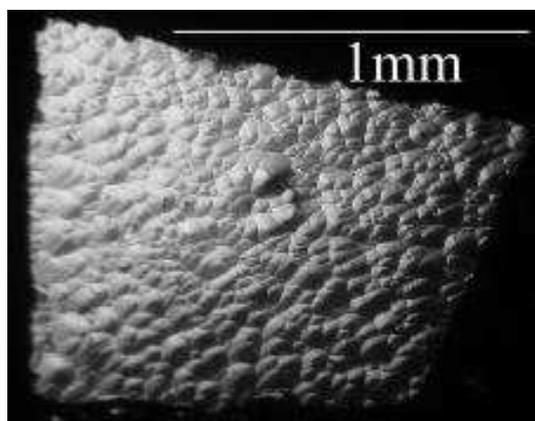


Fig. 4. Vicinal pyramids developed on {211} faces of the BGO crystal.

The real structure of BGO crystals depends on the crystal growth conditions resulting in distribution of impurities on growth sectors (Fig.5). There are two different types of six growth sectors because they belong to two crystallographic forms,  $\{110\}$  and  $\{112\}$ , which characterize by different segregation coefficients of impurities between liquid and solid phases.

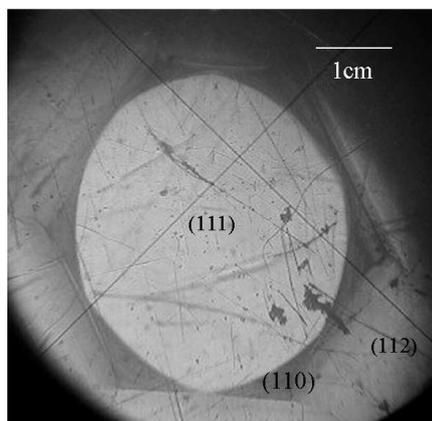


Fig. 5. Growth sectors in BGO crystal: a cut perpendicular to  $[111]$ .

Another typical defects of crystals grown on the seeds parallel to  $\{111\}$  are zones with gaseous-liquid inclusions as a result of temperature instability. Also, the instability of crystal growth conditions and a deviation of seed orientations from morphologically stable crystallographic directions lead to the formation of metastable phase inclusions.

As a result of absorption spectra measurements (Fig. 6), it can be concluded that colour of BGO crystals is due to  $\text{Cr}^{4+}$  and  $\text{Cr}^{5+}$  impurities arising from starting chemicals.

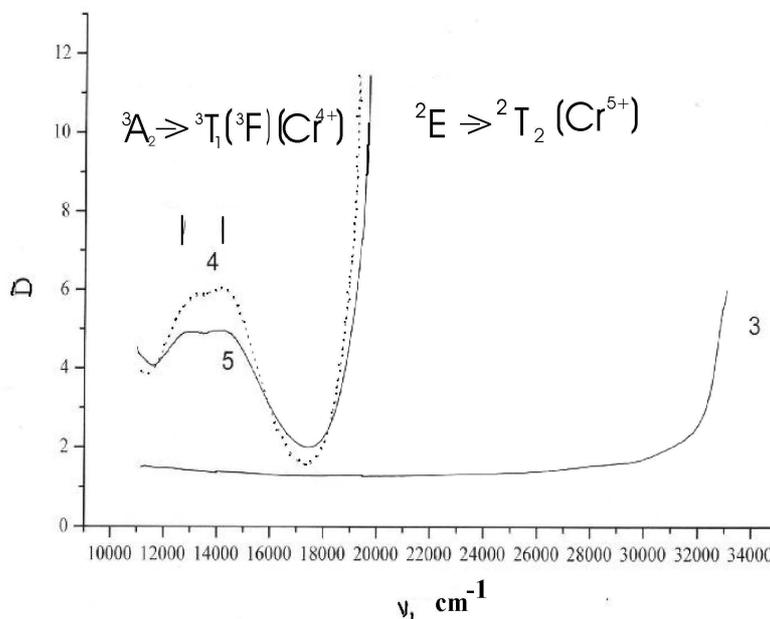


Fig. 6. Absorption spectra for BGO crystals.

On the whole, external and internal morphology of synthetic  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  and  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  crystals is similar to the natural eulytite, and it is an easy way for identification of the simple forms in this mineral.

#### 4. Conclusions

In this paper, visually homogeneous eulytite-type BSO and BGO crystals have been synthesized by spontaneous nucleation in hydrothermal  $\text{NH}_4\text{F}$ ,  $\text{HClO}_4$  and  $\text{KOH}$  solutions. BSO and BGO crystals have also been obtained on the seeds of Czochralski grown bismuth germanate. Growth rate of BSO and BGO crystals increases with increasing concentration of solvent, crystallization temperature and temperature gradient. The synthetic eulytite crystals tend to grow with strongly developed  $\{211\}$  and  $\{2\bar{1}\bar{1}\}$  faces. External and internal morphology of these synthetic eulytites is similar to their natural prototype, and it is an easy way for identification of the simple forms in this mineral.

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