Grain Size Trends and Correlation Analysis in Highly Ordered Grain Line Structure of Bismuth Silicate (Bi$_4$Si$_3$O$_{12}$) Micro-Crystals

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Abstract: Highly ordered bismuth silicate micro-crystals have been grown by sintering method at 800°C for the first time. The samples were characterized for structural and surface morphological properties by X-ray diffraction (XRD) and Environmental scanning electron microscopy (ESEM). The result shows that a pure cubic phase (Bi$_4$Si$_3$O$_{12}$) was obtained. The Bi$_4$Si$_3$O$_{12}$ grains always distribute in pairs on both sides and arrange grain lines. There are two types of grain size trend along with the growth direction of the grain line. One trend is gradually increased or decreased and the other trend is basically unchanged. In most cases the grain size trends on both sides of one line are approximately consistent and there is a highly positive correlation between the grain growth rates on both sides of one line. The highly positive correlation analysis indicates a relationship between grain growth rates on both sides, such as when the value for one grain growth rate increases, the value for the other grain growth rate in pairs also increases. If the grain size trends on both sides are thoroughly inconsistent and there is a nonlinear relationship between grain growth rates on both sides in one line, these two trends may belong to two types respectively.

Keywords: Bi$_4$Si$_3$O$_{12}$, Grain line, Grain size trend, Correlation coefficient growth rate

1. Introduction

There is an increasing interest in bismuth silicate Bi$_4$Si$_3$O$_{12}$ (BSO) and bismuth germanate Bi$_4$Ge$_3$O$_{12}$ (BGO) materials owing to their remarkable characteristics such as fast luminescent decay constant, large light output and radiation hardness [1-3]. These two compounds are used as high-efficient scintillators in gamma ray spectroscopy and high energy physics, and widely applied in non-linear optical devices and nuclear medicine (X-ray and positron computer tomography) [4-9].

BSO has an eulytite structure with point group 43 m, which is isomorphous to BGO crystals. Although resembling in many respects including physical, optical and scintillation characteristics, they exhibit obvious differences in some scintillation properties such as BSO has faster response and smaller light output than BGO. Apart from better scintillation properties, BSO has the advantage of a lower cost compared to BGO because of the cost of
high purity GeO₂ powder. Thus the BSO can be a preferable substitute for BGO in some fields [7-9]. Some studies have been reported on crystal growth and characterization of BSO single crystal [5-12]. To our knowledge, no paper has appeared on highly ordered Bi₄Si₃O₁₂ micro-crystals investigating the crystallizing behavior of Bi₄Si₃O₁₂ in the previous researches. Till now there have been no reliable data on the grain line structure of Bi₄Si₃O₁₂ crystallites.

In previous work, we have studied the morphology of the Bi₄Si₃O₁₂ crystals that differs under different thermal treatment. In this paper the highly ordered grain line morphology of Bi₄Si₃O₁₂ micro-crystals was analyzed. The characteristics of grain size trends and correlation in pairs of bismuth silicate (Bi₄Si₃O₁₂) micro-crystals are reported.

2 Experimental Procedure
2.1 Preparation of BSO crystals

Starting materials were Bi₂O₃ (monoclinic) powder (Analytical reagent, Tianjin No.3 Chemical Plant, Tianjin, P. R. China) and SiO₂ powder (Analytical reagent, Huzhou Chemical Reagent Factory, Zhejiang, P. R. China). Bi₂O₃ and SiO₂ were mixed in the mole ratio of 1:1, and then milled for 3 hours in ethanol at room temperature [13-15]. The mixture was dried under the infrared ray light (60W). The dried powders were heated at a heating rate of 10°/min to 800°C and held at this temperature for 3 hours in an Al₂O₃ crucible covered with a lid in air. The samples were cooled to the room temperature at a rate of 30°/min. (XRD shows that the raw Bi₂O₃ powder was monoclinic and the raw SiO₂ powder was amorphous.)

2.2 Characterization of the prepared crystals

The crystalline phases of the sintering samples were identified using X-ray Diffractometry (XRD, D/max 2200PC, CuKα irradiation, Rigaku, Japan). The morphology of the crystal surface was observed by Environmental Scanning Electron Microscopy (ESEM, Quanta 200, Philips-FET, Holland).

3 Results and Discussion
3.1 X-ray diffraction studies

Fig. 1 shows the X-ray diffraction pattern of the phase that appeared on the surface of the sample. It is clear from the analysis that the surface phase is Bi₄Si₃O₁₂ (JCPDS card No. 35-1007), with peaks of (211), (310), (321), (400), (422), (431), (532) and (710).
Fig. 1 XRD pattern of the sample
BSO has the eulytite structure with point group 43 m, and the structure can be considered as the reciprocal linkage of [SiO₄] tetrahedron and [BiO₆] octahedron in the space.

3.2 Morphological studies
3.2.1. Grain line structure

Fig. 2 shows the micrograph of the BSO crystallites. Fig. 3 is the enlarged image of the Bi₄Si₃O₁₂ micro-crystals in Fig. 2. A highly ordered grain line structure of BSO crystal grains is clearly exhibited in Fig. 3, in which each line of highly ordered crystals is identified with A-F, respectively (Fig. 3). It is obvious that the grains are always distributed in pairs on both sides and arrange grain lines.

Fig. 2 Micrograph of the highly ordered Bi₄Si₃O₁₂ micro-crystals

Fig. 3 Enlarged image of the Bi₄Si₃O₁₂ micro-crystals in Fig. 2

The growth direction of Line A is along the arrow ‘P’, and the growth directions of Line A-F (the arrows in Fig. 3) are approximately parallel. According to the growth characteristics of BSO in Fig. 3, the exposed crystal faces were {204} faces. When the {124} faces of one grain met with the similar planes of other two grains on the same side of one line, the {124} faces of adjacent grains bond together by coplaner based on the identical growth
habit. With grain growth, the \{124\} faces gradually die out and the highly ordered grain line structure was formed.

3.2.2. Basic statistics

The measured length \(l\) in Fig. 3 is the distance between two intersection points of the crystal faces \{204\} and \{024\}. A total of 392 grains were measured. The basic descriptive parameters of mean, standard deviation, difference percentage between means on both sides are shown in Tab.1.

**Tab. 1** The descriptive statistics of grain size of Line A-F presented in Fig.3 (L and R are left and right sides of one line respectively)

<table>
<thead>
<tr>
<th>Line</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Side</td>
<td>L</td>
<td>R</td>
<td>L</td>
<td>R</td>
<td>L</td>
<td>R</td>
</tr>
<tr>
<td>Mean (l) ((\mu m))</td>
<td>1.44</td>
<td>1.98</td>
<td>0.59</td>
<td>0.81</td>
<td>1.28</td>
<td>0.83</td>
</tr>
<tr>
<td>Standard Deviation (\sigma) ((\mu m))</td>
<td>0.17</td>
<td>0.16</td>
<td>0.19</td>
<td>0.20</td>
<td>0.14</td>
<td>0.19</td>
</tr>
<tr>
<td>Difference Percentage (%)</td>
<td>26.6</td>
<td>27.1</td>
<td>33.5</td>
<td>37.9</td>
<td>26.4</td>
<td>21.5</td>
</tr>
</tbody>
</table>

\(\frac{|\overline{l_L} - \overline{l_R}|}{\text{Max}(\overline{l_L}, \overline{l_R})} \times 100\%\)

The raw data exhibits a wide range of grain size variation of several magnitudes among the lines, which shows the mean of grain size is from 0.59 \(\mu m\) to 2.03 \(\mu m\), showing the strong diversity of grains in the lines. The difference in percentage between means of grain size on both sides of one line is from 21.5% to 37.9%, and the difference level is significant.

3.2.3. Grain size change trends

Fig. 4 shows the grain size (length) change curves in Line A, B, C, D, E, and F. From fig. 4(a) it represents the grain size change trend on each side that gradually decreases along with the growth direction (the arrow 'P') of Line A, and these two change trends are basically consistent. Fig 4(b) shows that the grain size change trend on each side is gradually increased along with the growth direction of Line B, and the two change trends are basically similar. Although the means of grain size on both sides of Line A are almost two times of those of Line B respectively (Tab.1), the conformance of the grain size change trends of the grains on both sides is nearly same. In Fig.4 (c), the grain size trend on each side is gradually decreased along with the growth direction (the arrow) of Line C, and two change trends are approximately consistent. Compared with Line A and C, the grain size trends on both sides of Line B are opposite to those of Lines A and C, but the variation rate is basically similar. Although the means in Line A are significantly higher than the other lines, the conformance of the grain size change trends on both sides is approximately the same. The phenomenon
exhibited that the conformance of the grain size change trends may be the wonderful crystal habit of Bi$_4$Si$_3$O$_{12}$ micro-crystals.

In Fig. 4 (d), the grain size trend along with the growth direction of Line D on each side remains basically unchanged in a narrow region, and these grain size trends on both sides are almost consistent. In Fig. 4 (e), the grain size on each side also keeps basically unchanged trend, and two grain size trends are also approximately consistent. Compared with Line A-E, it can be found that there are two types of grain size trend. One trend is gradually increased or decreased, e.g. on each side of Line A, B, C. The other trend is basically unchanged, e.g. on each side in Line D, E. These trends can be considered basically as two types of increased (decreased) or unchanged, the conformance of the grain size change trend on both sides is approximately similar.

**Fig. 4** The curves of grain size change in Line A-F
The grain size trends on both sides of Line F show a significant difference in Fig. 4 (f). Grain size on left side represents the same trend type with that on each side of Line D, E. The grain size on the right side shows the same trend type with that on each side of Line A-C. These two trends are completely inconsistent in Line F, and the reason is explained that there may be other factors that greatly affect the BSO crystal growth on left side.

3.2.4. Correlation analysis

In order to further investigate the relation of the crystal grains on both sides in each line, statistical methods are used to calculate the correlation coefficient between grain sizes on both sides of each line. The correlation coefficient (R), measures the strength and the direction of a linear relationship between two variables. The mathematical formula for computing R is:

\[
R = \frac{n \sum l_i l_R - \sum l_i \sum l_R}{\sqrt{n \sum l_i^2 - (\sum l_i)^2} \cdot \sqrt{n \sum l_R^2 - (\sum l_R)^2}}
\]

Here \( l_i \) and \( l_R \) are grain sizes on the left and right sides, respectively, and \( n \) is the number of pairs of crystal grains in one line. The value of R is such that \(-1 \leq R \leq +1\). The + and - signs are used for positive linear correlations and negative linear correlations, respectively. The correlation coefficients between grain sizes on both sides in the lines (Line A-F) were analyzed (in Tab. II).

<table>
<thead>
<tr>
<th>Line</th>
<th>A</th>
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<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
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<tbody>
<tr>
<td>R</td>
<td>+0.76</td>
<td>+0.82</td>
<td>+0.87</td>
<td>+0.76</td>
<td>+0.7</td>
<td>-0.09</td>
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From Tab. II, \( R_A = +0.76 \), \( R_B = +0.82 \), \( R_C = +0.87 \), \( R_D = +0.76 \), \( R_E = +0.70 \), are greater than or equal to 0.7, show that there is a highly positive correlation between grain sizes on both sides of one line (Line A-E). The data shows a relationship between grain sizes on both sides, such as value for left grain size is larger, value for right grain size (in pairs) is also larger. In other words, as value for left grain growth rate increases, value for right grain growth rate (in pairs) also increases. The value R in Line F is close to zero, it shows that there is a nonlinear relationship, and the reason for this is that there may be other factors that greatly affect the BSO crystal growth. Additionally, as the structure is isomorphous to BSO crystals, BGO probably has a similar crystallization habit with highly ordered grain line structure and correlation characteristics.

4. Conclusions

Pure cubic \( \text{Bi}_4\text{Si}_3\text{O}_{12} \) micro-crystals were prepared by a sintering method at atmospheric pressure and cooled to room temperature in air. The grains are always distributed in pairs and arrange grain lines. There are two types of grain size change trends along with the growth direction of one line. One trend is gradually increased or decreased, and the other trend is basically unchanged in a narrow region. These two trends of grain size on both sides of each line are basically consistent in Line A-E. The correlation coefficients between grain sizes on both sides in Line A-E are 0.76, 0.82, 0.87, 0.76 and 0.70, respectively. There is a highly positive correlation between grain sizes on both sides in these lines. The result
indicates a relationship between grain sizes on both sides such that as value for left grain size is larger, value for right grain size (in pairs) is also larger. In other words, as the value for the left grain growth rate increases, the value for the right grain growth rate (in pairs) also increases. The grain size trends on both sides show a significant difference in Line F. Grain size on left side represents the same trend with that on each side of Line D,E. Grain size on right side shows the same trend with that on each side of Line A-C. In most case, the grain size trends on both sides are approximately consistent and there is a highly positive correlation between the grain growth rates on both sides of one line. If the grain size trends on both sides are thoroughly inconsistent and there is a nonlinear relationship between grain growth rates on both sides in one line, these two trends may belong to two types respectively. In addition, as the structure is isomorphous to BSO crystals, BGO micro-crystals probably have a similar crystallization habit with a highly ordered grain line morphology.

Acknowledgements

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References


Садржај: Методом синтеза на 800°С добијени су први пут веома добро структурно организовани микро кристали бизмут силиката. Структурна и површинска морфолошка својства узорака су карактерисана коришћењем рентгенске
дифракције и просторне скенирајуће електронске икроскопије. резултати су показали да је добијена чиста кубична фаза Bi₄Si₃O₁₂. Bi₄Si₃O₁₂ зrna су увек распоређена у паровима на обе стране и формирају линије зrna. Постоје два тренда промене величине зрна у правцу раста линије зрна. Један је постепено увећање или смањење а други тренд је практично непромењен. У већини случајева трендови раста зрна на обе стране једне линије су приближно конзистентни и постоји високо позитивна корелација између брзине раста зрна на обе стране. Високо позитивна корелациона анализа указује на везу између брзине раста зрна на обе стране јер када једна вредност брзине раста зрна расте, расте и друга у пару. Ако су трендови промене величине зрна на обе стране различити онда постоји нелинеарна веза између брзине раста зрна на обе стране једне линије и ови трендови су различитог типа.

Кључне речи: Bi₄Si₃O₁₂, линија зrna, тренд промене величине зrna, корелациони коефицијент брзине раста.