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Raman Spectrum Analysis on the Solid–Liquid Boundary Layer of BGO Crystal Growth *

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We study the Raman spectra of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystal at different temperatures, as well as its melt. The structure characters of the single crystal, melt and growth solid–liquid boundary layer of BGO are investigated by their high-temperature Raman spectra for the first time. The rule of structure change of BGO crystal with increasing temperature is analysed. The results show that there exists $[\text{GeO}_4]$ polyhedral structure and Bi ion independently in BGO melt. The bridge bonds Bi–O–Bi and Bi–O–Ge appear in the crystal and at the boundary layer, but disappear in the melt. The structure of the growth solid–liquid boundary layer is similar to that of BGO crystal. In the melt, the long-range order structure of the crystal disappears. The thickness of the growth solid–liquid boundary layer of BGO crystal is about $50\ \mu\text{m}$.

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$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) single crystal is an excellent scintillation crystal and has been widely used in high-energy physics, space science, medical imaging.^[1,2] Two different Czochralski (Cz) methods have been used to grow BGO crystals. The common one is the conventional Cz method, in such a way, high temperature gradient is applied to achieve the fully rounded solid–liquid interface. The alternative method is the low temperature gradient (LTG) Cz method, in such a way, the temperature gradient is small and the rounded solid–liquid interface changes to the polyhedral growth interface shaped with $\{211\}$ faces. BGO crystal has a pronounced tendency of facet growth, with fully faceted stable interface. It is possible to obtain high-quality uniform BGO crystals free of inclusions. However, if any deviations from optimal conditions take place, the planes $\{211\}$ lose their stabilities, the solid–liquid interface is composed of both rounded and faceted parts.^[3] In these cases, various mechanisms of growth may occur on the solidification interface, which result in the formation of defects on their borders and significant deterioration of the properties of BGO crystals. Therefore, it is necessary to study the growth mechanism of BGO crystal.

Crystal growth is a complicated interface process. Bilgram *et al.* supposed that a meso-phase layer presents in front of a growing crystal in the process, the crystal does not grow into the bulk melt, but into the meso-phase.^[4] The liquid-phase near solid–liquid interface plays an important role in the formation of growth units, surface kinetics and crystal growth mechanism.^[5–7] We call this characteristic region the boundary layer of crystal growth. The research of the boundary layer can explain the growth process of crystals and is helpful to study the crys-

tal growth mechanism further. In this study, we use a high temperature Raman spectrometer to probe *in situ* the structure of the solid–liquid boundary layer of BGO crystal growth. Furthermore, we investigate the growth mechanism of BGO crystal.

BGO crystal used in this study was grown from a stoichiometric melt by the Czochralski method in a platinum crucible. The BGO sample with the size of $5 \times 10 \times 1.2\ \text{mm}^3$ was cut from the mother crystal along the $[100]$ direction, then, the crystal surface was polished to optical quality for Raman spectra measurement. This sample was placed into a Platinum crucible in a micro crystal growth cell^[8] which has three-dimensional temperature gradient. The temperature was controlled by the A1-808P temperature micromanipulator with the control precision 0.1 K. By carefully controlling the temperature, the crystal and melt keep a dynamical equilibrium, and a steady crystal growth solid–liquid interface can be obtained.

In the experiments, the Raman spectra at different temperatures were recorded with a JY U1000 Raman spectrometer in a back scattering configuration.^[9,10] The excitation source was the 532 nm line of a Q-switch pulsed SHG-Nd:YAG laser. An intensive charge couple device (ICCD) was equipped as the detector system. The diameter of the light beam was less than $2\ \mu\text{m}$. The laser beam was focused in turn on the different positions around the solid–liquid interface. The detecting position could be selected by a computer monitor. The Raman scattering light was collected by a back-scattering confocal lens system, and led into the monochromator with an entrance slit of $300\ \mu\text{m}$, then collected by the ICCD at the outlet slit. The typical instrumental resolution was $\pm 1\ \text{cm}^{-1}$ with repeatability $\pm 0.1\ \text{cm}^{-1}$.

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$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystal belongs to the $I\bar{4}3d$ space group with four formula units in the crystallographic unit cell. The atomic arrangement is characterized by isolated tetrahedral $[\text{GeO}_4]$ and distorted octahedral $[\text{BiO}_6]$. The primitive unit-cell contains $n = 38$ atoms, leading to $3n - 3 = 111$ optical branches at $K = 0$, they are classified as $\Gamma = 4A_1 + 5A_2 + 9E + 14F_1 + 14F_2$. Among them, 27 modes ($4A_1 + 9E + 14F_2$) are Raman active, while the modes are infrared active.^[11]

The observed Raman spectrum of BGO crystal at room temperature is shown in Fig. 1. It consists of nine frequencies (139 cm^{-1} , 163 cm^{-1} , 197 cm^{-1} , 239 cm^{-1} , 357 cm^{-1} , 396 cm^{-1} , 440 cm^{-1} , 717 cm^{-1} , 817 cm^{-1}) for the tetrahedral $[\text{GeO}_4]$ vibrations, two frequencies (119 cm^{-1} , 262 cm^{-1}) for the Bi–O–Bi and Bi–O–Ge bridge bond vibrations and one frequency (86 cm^{-1}) for Bi, O and Ge ion vibrations. The frequencies of observed Raman spectra and their possible assignments are listed in Table 1.

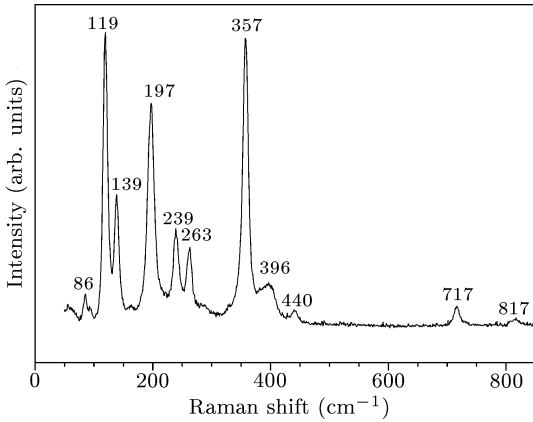


Fig. 1. Raman spectrum of BGO at room temperature.

Table 1. Raman frequencies of BGO crystal and their assignments.

| Frequency (cm^{-1}) | Possible assignment |
|--------------------------------|---------------------------------|
| External modes: | |
| 86 | Bi, O and Ge vibrations |
| 119 | Bi–O–Ge bond bending |
| 139 | GeO_4 translations |
| 163 | |
| 197 | Ge–O bond rocking, O-localized |
| 239 | GeO_4 rocking |
| 263 | Bi–O–Bi and O–Bi–O bond bending |
| 357 | GeO_4 rotation |
| Internal modes: | |
| 396 | O–Ge–O bond bending |
| 440 | |
| 717 | Ge–O bond stretching |
| 817 | |

Figure 2 shows the Raman spectra of BGO crystal from room temperature to its melting point (1323 K). With temperature increasing, all of the Raman peaks shift to low frequencies and broaden in different degrees. This means that the corresponding bond lengths between atoms increase, and

the effort among atoms decreases with temperature increasing.^[12] The peaks located around 120 cm^{-1} , 200 cm^{-1} and 320 cm^{-1} can be obviously observed, they are attributed to the tetrahedral $[\text{GeO}_4]$ vibrations, implying that $[\text{GeO}_4]$ tetrahedron exists in both the crystal and its melt. The peaks located at 110 cm^{-1} and 263 cm^{-1} disappear in the melt. They are attributed to the bridge band Bi–O. This means that the Bi–O bond broke in the melt. The Bi–O bond is ionic bond and weaker than the Ge–O bond in BGO crystal. When the crystal melts, the Bi–O bond is broken first, i.e. the long-range order crystal structure is broken. It can be believed that there exist $[\text{GeO}_4]$ tetrahedrons and Bi ions independently in the melt.

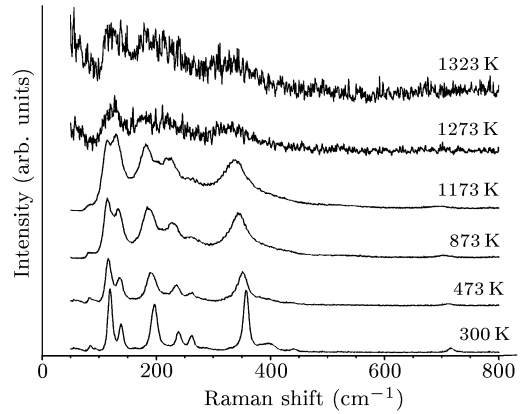


Fig. 2. High-temperature Raman spectra of BGO crystal and the melt.

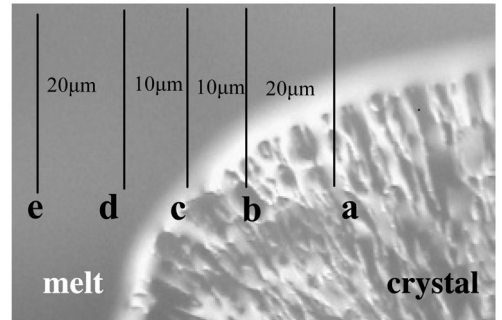


Fig. 3. Positions of measuring points and solid-liquid boundary layer of BGO crystal.

The laser beams were focused in turn on the crystal and the melt around the solid-liquid interface (see Fig. 3), the Raman spectra at different positions are obtained, as shown in Fig. 4. The vibration frequencies of the tetrahedral $[\text{GeO}_4]$ (129 cm^{-1} , 183 cm^{-1} , 220 cm^{-1} , 321 cm^{-1}) and the vibration frequencies of the bridge band Bi–O (110 cm^{-1} , 248 cm^{-1}) can be observed in the characteristic boundary layer, as shown in Fig. 4(c). The peak position of those bands decreases in different degrees, compared with those peaks of the crystal (see Fig. 4(a) and (b)). It is proven that $[\text{GeO}_4]$ tetrahedrons exist in the boundary layer,

and connect each other by the Bi–O bridge bond. The character structure of the growth units in the boundary layer is similar to the structure of the crystal.

The Bi–O–Bi and O–Bi–O bond vibration and the Bi–O–Ge bond vibration disappear in the melt (see Figs. 4(d) and 4(c)). $[\text{GeO}_4]$ tetrahedrons and Bi^{3+} ions become two independent units. Here we propose the structural model for the combination reaction occurring in the BGO solid–liquid boundary layer. It is approved that during the crystal growth process, tetrahedral $[\text{GeO}_4]$ was connected by the bridge bond step by step to form the growth unit in the boundary layer, and the growth units of the crystal are the same as the anion-coordination polyhedral in the crystal.^[13]

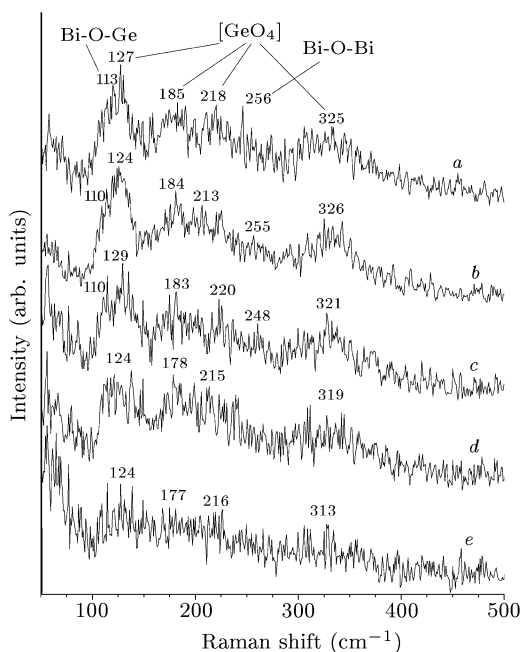


Fig. 4. Raman spectra of crystal [(a) and (b)], boundary layer (c), and melt [(d) and (e)] at the same temperature slightly lower than the melting point. Curves a–e correspond to the measurements at the points a–e shown in Fig. 3.

The growth characteristics of BGO crystal can be explained based on the above result. In general, the shape of a crystal is determined by the relative rates of deposition of crystal growth units on its various faces, the faces that grow slowest appear to be large developed faces.^[14] The growth rates are determined primarily by the strength of binding of the particles which arrive at several crystal surfaces, the slowest growing, and hence largest faces are those with the weakest strength of binding.^[15] From the above experimental results, we know that the weakest bond in the BGO crystal is the Bi–O bridge bond. Along the $\langle 211 \rangle$ orientations the growth units are connected by the Bi–O bridge bond (see Fig. 5), so the corresponding faces grow slowly and strongly exposed. Thus, during the growth of the BGO crystal, the facets $\{211\}$ are easily exposed. It is always seen that the decrease of con-

vexity of the interface is followed by the increase of facets $\{211\}$.^[16]

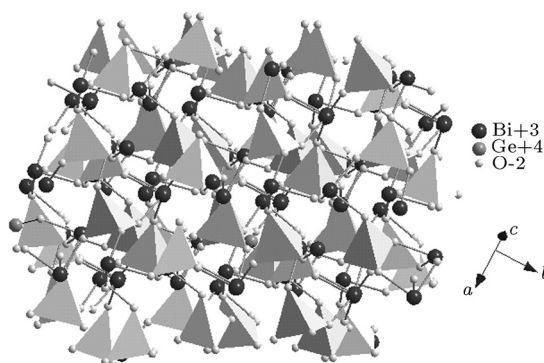


Fig. 5. Projection of BGO crystal at a (211) face.

The thickness of the boundary layer is different for different crystallizing materials, crystal structure, growth mechanisms and so on.^[6] By the *in situ* observation and the location at which the bridge bonds of Bi–O–Bi and Bi–O–Ge disappear, the thickness of the growth boundary layer of BGO is proven to be about $50 \mu\text{m}$, for the first time.

In summary, as far as BGO crystal is concerned, the Bi–O–Bi and Bi–O–Ge bridge bonds exist in the crystal and at the boundary layer, but disappear in the melt. The $[\text{GeO}_4]$ tetrahedrons and Bi ions exist independently in the melt, and the long-range order structure of the crystal disappears. In the boundary layer, $[\text{GeO}_4]$ tetrahedrons are connected by the bridge bonds step by step to form the growth units. The structure of the boundary layer is more similar to the structure of the crystal than the melt. The thickness of the boundary layer of BGO crystal is proven to be about $50 \mu\text{m}$.

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