Influence of microgravity on Ce-doped $\text{Bi}_{12}\text{SiO}_{20}$ crystal defect

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Abstract. Space grown BSO crystal doped with Ce was characterized by means of X-ray fluorescence spectra, X-ray topography, dislocation density etc. Influence of microgravity on Ce-doped BSO crystal defect was studied by comparing space grown BSO crystal with ground grown one. These results show that compositional homogeneity and structural perfection of crystal can be improved under microgravity conditions.

Keywords. Oxides; crystal growth; microgravity; dislocation.

1. Introduction

Bismuth silicon oxide, $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) crystal, has a body centred cubic structure with space group, $I23$ and melt congruently at about 895°C. This material is very attractive for practical applications due to its pronounced piezoelectric, electro-optic, acousto-optic and photorefractive properties (Aldrich *et al* 1971; Peltier and Micheron 1977; Grousson *et al* 1984; Stepanov *et al* 1987). Therefore, BSO is a potential material for real-time optical information processing, optical computing, real-time interferometry and image amplification (Lipson and Liscenson 1974). BSO crystal with a variety of dopants such as Al, Mn, Ce etc has been investigated in order to improve and increase its range for applications (Fan 1994; Gospodinov *et al* 2000). Doped BSO crystals, in general, by Czochralski (Tanguay *et al* 1997) or Bridgman method (Xu *et al* 1993), have some defects such as inhomogeneity of dopant, growth striations, darkened cores and twinning and so on. In order to improve the quality of BSO crystals, Ce-doped BSO crystal was grown under microgravity conditions on board the Chinese Spacecraft—Shenzhou No. 3.

In this paper, Ce doped BSO crystal for space growth has been analysed by chemical etching, X-ray topography and X-ray fluorescence spectra. Macro- and microscopic defects of doped BSO crystal are presented. The effect of microgravity conditions on defect formation and dopant segregation during crystal growth is studied.

2. Experimental

The Ce doped BSO crystals were grown by the Bridgman method in space or on earth and the corresponding experi-

mental details can be found in Zhou *et al* (2004). BSO crystals were directional in the beginning and then cut to several plates parallel to (111) and (110) faces, respectively. Chemical etching of the cut and polished (111) plates, what were in later parts of crystal, was accomplished. Specimens were etched in 3M HCl solution for 3 min at room temperature.

Synchrotron white beam X-ray topography (SWBXT) (Dudley 1994) is a non-destructive technique that can be used to rapidly characterize structural defects such as dislocations, precipitates/inclusions, growth sector boundaries, etc and low defect density crystals that are distorted and/or contain twinned regions. Structural defects and their type are revealed by contrast arising from interaction of the X-ray beam with distortions of the diffracting lattice planes caused by the strain fields surrounding the defects. The broad wavelength range of the white radiation can be used to identify crystallographic orientation relationships through Laue diffraction patterns. SWBXT and X-ray fluorescence (XRF) were carried out at Beijing Synchrotron Radiation Laboratory (BSRL). The samples polished parallel to growth direction were thin enough (500 μm) slices of (110) face to permit the use of transmission geometry.

3. Results and discussion

3.1 Surface view

Figures 1(a) and (b) show partly space-grown and ground-grown BSO crystals (Φ 10 mm in diameter), respectively. The surface of space crystal is glossy, especially near the later part of crystal growth, but the ground crystal has some concave grooves on the surface. Macroscopic defects of surface of ground grown crystal results from sticking of BSO melt to Pt crucible. The morphological differences between space- and ground-crystal may be due to detached

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growth of BSO crystal in space, however, there is partial wetting between Pt crucible and BSO melt on earth (Zhou et al 2004).

3.2 Dislocation etching

Dislocation etch pit density (EPD) of BSO crystal is the average number of etch pits observed in the area of sample by an optical microscope. Figure 2 shows the etch patterns of centre areas of Ce doped crystals. The average EPD of centre area of space grown crystal on (111) slice is $5 \times 10^2 \text{ cm}^{-2}$, compared to $6.5 \times 10^3 \text{ cm}^{-2}$ for the ground grown one. The EPD of space crystal is one order of magnitude less than that of ground crystal. The reduction of EPD in space-grown specimen may be a result of changes in shape and composition at solid-liquid interface. The shape of interface changes from concave to convex by suppressing convection in the melt, and such a change is useful for reducing crystalline defects (Nikitenko and Indenbom 1961; Brice 1968).

Figure 3 shows the etch patterns of areas near the crucible of Ce doped crystals. The EPD of space crystal is less orders of magnitude than that of ground crystal. The result is attributable to detached growth in space. As figures 2(a) and 3(a) show, the EPDs of space crystal, whether the radial centre part or near the crucible wall, have seldom any variation. However, dislocations of ground crystal near the crucible surface gather easily together the dislocation bundles, as shown in figure 3(b). The reason for the obvious increase of dislocation density near crystal edge is that the high stress caused by adhesion of a ground-grown crystal to its crucible wall causes multiplication of dislocations.

Figure 1. Parts of Ce doped BSO crystals: (a) space growth and (b) ground growth.

3.3 Synchrotron topography

The synchrotron transmission topographs of space and ground BSO crystals on (110) slices are shown in figure 4. Dislocation lines, both straight and curved, mostly parallel to growth direction, are observed in space- and ground-grown crystals. Some surface scratches (*S*) are also observed because hardness of BSO crystal is low. The first ones, *D_g*, both space and ground crystal, correspond to dislocations propagated from the crystal growth front. The second type of dislocations, *D2*, is a cluster of dislocations originating from the border of ground crystal. It is indicative of a high level of strain at the boundary, which arises from Pt crucible sticking with the border of ground crystal. Similar *D2* dislocations of ground crystal are not found near the edges of space crystal. Faint contrast area of space crystal can be attributed to temperature fluctuation during the space growth process.

Figures 5 and 6 show X-ray topographs of space and ground crystals during initial growth process. Twin (*T*) regions, either space- or ground-crystal, are observed clearly. Defects of the seeding part were seen by direct eye contact while inspecting the polished samples.

Figure 2. Etch patterns of centre areas on the (111) faces: (a) space-grown, EPD = $5 \times 10^2 \text{ cm}^{-2}$ and (b) ground-grown, EPD = $6.5 \times 10^3 \text{ cm}^{-2}$.

The distortion interferogram (Zhou *et al* 2004) of seeding region of space sample showed twinning defects. The defects of seeding region could be attributable to the axial thermal fluctuations and compositional variation due to the increase of Ce impurity concentration in the seeding process. The reason for twin formation is less clear. The solid–liquid interface shapes as shown in figures 5 and 6 are very different for space- and ground-grown crystals. One is a concave interface for space crystal and the other is a convex interface for ground crystal. The starting crystal growth with slight concave interface is due to reducing convection in the melt under microgravity environment.

3.4 Ce concentration variation

The Ce concentration data along growth direction of crystal obtained by XRF analysis is a relative variation value due to no standard sample as comparison. Ce concentration of the starting growth (head) measured space and ground crystal as reference point 1, respectively, figure 7 shows Ce relative concentration variation along crystal growth direction. Figure 7 indicated that the effective segregation

coefficient, K_{eff} , of Ce doping is < 1 . The Ce concentration in the tail of space-grown crystal is about 10% higher than that in the head. The Ce concentration relative variation for tail and head of ground-grown crystal is about 35% higher than those compared to Ce concentration variation of space grown crystal. The Ce segregation takes place during the crystal growth that leads to the gradual increase of the Ce concentration and the formation of a Ce-rich thin layer near interface. During the space crystal growth, a Ce-rich thin layer near interface is almost stable

Figure 3. Etch patterns near crucible edges on the (111) faces: (a) space and (b) ground.

Figure 4. X-ray topographs of (110) slices: (a) space, $(\bar{3}21)$ diffraction, (b) space, $(\bar{3}50)$ diffraction, (c) ground, $(\bar{3}21)$ diffraction and (d) ground, (105) diffraction.

Figure 5. X-ray topograph of space on $(3\ 2\ 1)$ face diffraction during initial growth process.

Figure 6. X-ray topograph of ground on $(1\ 0\ 5)$ face diffraction during initial growth process.

Figure 7. The Ce concentration distribution along growth direction of crystal.

because the solute and thermal convection are validly suppressed. The Ce axial concentration variation of crystal in space growth is smaller than that of ground grown

crystal, especially at the middle and later periods of crystal growth.

4. Conclusions

Some defects of doped BSO with Ce crystals between space growth and ground growth, such as concave pits of crystal surface, dislocation etching pits, dislocation lines and twinning, were studied and discussed. Detached growth of doped BSO with Ce under microgravity conditions can avoid the wetting of Pt crucible and BSO melting, decrease obviously dislocation clusters coming of thermal stress of crystal surface. The differences in the EPD near the crucible wall between the space- and ground-grown crystals also proved that detached growth in space is useful for increasing crystallographic perfection. The Ce distribution along crystal growth direction differed obviously in microgravity and on earth which is explained by different Ce segregation efficiencies. On doping with Ce, compositional distribution of space crystal was more homogeneous than that of ground crystal. The result showed the benefits of suppressing convection for doped BSO crystal growth in microgravity.

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