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Energy spectrum analysis and growth of ZnTe: Cu under Microgravity on TG-2 spacecraft

WANG Reng, LU Ye[1], JIAO Cui-Ling, QIAO Hui, LI Xiang-Yang

(Key Laboratory of Infrared Imaging Materials and Detectors, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China)

Abstract: The ZnTe: Cu crystals grown under microgravity and on ground are characterized by optical and energy dispersive spectrum analysis. The radial and axial spectra of the largest crystal at the end of the ingot are analyzed. For the axial component of the tail section, the compositional uniformity of Cu in the space sample is better than that of the ground sample, and the Te/Zn ratio of the ground sample is higher than that of the space sample. The radial compositional uniformity of Cu in the space sample of the tail section is better than that of the ground sample, and the Te segregation of the ground sample is more serious.

Key words: microgravity, ZnTe: Cu crystal, energy dispersive spectrum analysis
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天宫二号 ZnTe: Cu 晶体生长及能谱分析

王 仍, 陆 液, 焦翠灵, 乔 辉, 李向阳

(中国科学院上海技术物理研究所 红外成像材料与器件重点实验室, 上海 200083)

摘要: 在微重力条件下生长了 ZnTe: Cu 晶体, 对其进行了光学和能谱分析, 在晶锭尾部最大结晶区对其进行了组分分析. 对于尾部的轴向分量, 在空间样品中 Cu 的成分均匀性优于地面样品, 并且 Te/Zn 比的样品高于空间样品. 尾部空间样品中 Cu 的径向成分均匀性优于地面样品, 且 Te 偏析更为严重.

关 键 词: 微重力; *ZnTe*: *Cu* 晶体; 能谱分析

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Introduction

The bandgap of ZnTe at room temperature is 2.26 eVs [1]. As a semiconductor material with II-VI sphalerite structure, the melting point is relatively high (about 1300°C), while the thermal conductivity are low. Therefore, it is very difficult to grow ZnTe material with large size and good crystal quality [2].

Growth methods of ZnTe crystal mainly include liquid sealed foaming method, gas phase method [3], melt method, and solution method which comprise Zn solvent and Te solvent methods. The equipment of liquid-sealed bubbled production method is expensive and material synthesis and growth need to be carried out at high temperature and high pressure furnace. Although the growth rate of Te solvent method is relatively slow [4], it can reduce the melting point temperature which makes it easier to get high-quality crystal materials.

According to the phase diagram, the growth of Group II-VI semiconductor materials using Te solvent method can effectively reduce the melting point, and the Te solvent method also has the purification effect which can improve the electrical parameter of the material. However, the specific gravity segregation and natural convection led to negative effects on crystal properties such as the uniformity of components for the material growth of the ground [5]. By contrast the growth of space can provide an effective way to solve these problems due to the microgravity environment [6]. In recent years, II-

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Biography: WANG Reng (1980-), female, Shandong Province, Ph. D. Research is mainly about II-VI semiconductor photoelectric materials and devices. E-mail: rwang@mail.sitp.ac.cn
* **Corresponding author:** E-mail: luye@mail.sitp.ac.cn

VI semiconductor materials have been grown under microgravity on home and abroad to overcome the inevitable gravity and convection effects on the ground. In space microgravity, natural convection disappears, and the crystal growth process is controlled by diffusion, which is very beneficial to improving the crystal quality. The growth of II-VI semiconductors under microgravity has been given more attention at home and abroad, such as HgCdTe, HgZnTe, CdZnTe, ZnSe, etc. At present, the research on the growth of ZnTe crystal growth in microgravity condition is still blank [7]. The Shanghai Institute of Technical Physics of the Chinese Academy of Sciences used the Temperature Gradient Solvent Growth Method (TGSG) to grow CdZnTe crystals on SZ-2 spacecraft and SZ-3 spacecraft, and obtained CdZnTe crystal growth of SZ-3 spacecraft at microgravity condition [8].

In 2013, ZnTe: Cu single crystals were successfully grown in the ground simulative experiment of TG-2 by SITP, as shown in Figure 1. Orange ZnTe crystals can be seen on the surface of the sample, indicating that the growth temperature and thermal control process can satisfy the melting point and growth condition of ZnTe crystal.

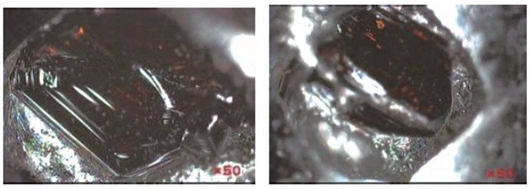

Fig. 1 ZnTe single crystal photographs
图 1 ZnTe 晶体照片

From October 3 to October 7, 2016, the sample was tested for crystal growth in the TG-2 spacecraft experiment device [9]. The experiment proceeded successfully as planned and the sample was brought back to the ground by the astronauts on November 18, 2016. In this experiment, ZnTe crystals were first grown by Te solution in space microgravity on the TG-2 spacecraft laboratory. After the flight experiment, the same experimental parameters were used on the ground sample [10]. The samples of ground experiment and the space experiments are from the same batch. In this paper, the effect of microgravity on crystal quality will be studied by comparing two experiments. Also the growth experience in space could be used to improve the growth of ZnTe and other II-VI semiconductor materials on the ground.

1 Experimental principle

Copper-doped ZnTe crystals were grown by the Te solution method in the six-section furnace on the TG-2 spacecraft. The six-position furnace was heated by two sets of furnace filaments and the growth temperature was as high as 800℃. In the space experiment, after the sample ampoule entered to the furnace, the ampoule was first lowered to the head of the crucible, which corresponding to the highest temperature position of the six-section furnace, heated to 800℃ and maintained for 60mins. The crystal was grown at the speed of 0.5 mm/hs to the interior of the furnace, the pure crystal growth time was about 90 h, and the actual crystal growth length in space was 45 mms. The total space experiment time was not less than 5 977 mins (~99.6 h). After the growth, the furnace was turned off and the ampoule was pulled out at the fastest speed (100 mm/h). The temperature gradient of the furnace was 10℃/cm. The effects of microgravity on the distribution of components were analyzed by comparing the radial and axial distribution of crystal compositional uniformity of the space sample and the ground sample.

2 Results and discussion

2.1 Analysis of Head Crystallization of Space and Ground samples

After the experiments on space and ground, the surface crystallization of the head and tail of the sample was first analyzed. From the head, the space sample (see Figure 2a) has a large crystal area with obvious holes. Orange ZnTe crystals were grown at the holes of the ingot. The ground crystallization region (see figure 2b) was small, so the head crystallization of the space sample was significantly better than the ground sample.

Fig. 2 Head comparison of the space and ground samples (a-space, b-ground)
图 2 空间样品和地面样品头部区域(a) 空间,(b) 地面

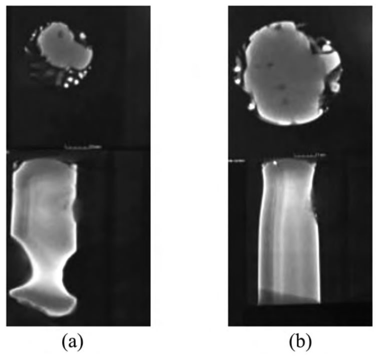

Fig. 3 Comparison of head sections of space and ground samples (X-ray CT scan-3D) (a-space, b-ground)
图 3 空间样品和地面样品头部区域 X 射线 CT 扫描-3D(a) 空间,(b) 地面

Figure 3 gives the comparison of head sections of space and ground samples. In the photograph, the dark section is ZnTe(ρ_{ZnTe} = 6.34 g/cm^3) crystal and the bright section is Te(ρ_{Te} = 6.24 g/cm^3). The 3D X-ray CT scan clearly shows that the crystalline area of the space sample is larger than the ground sample crystal area. Although the crystal region of the head of the space sample is larger than that of the ground sample, its crystal size is small, but the tail crystal size is relatively large. The detailed analysis will be shown in section 3.2.

2.2 Analysis of Tail Crystallization of Space and Ground Crystals

At the tail of the space sample (Fig. 4), there is a very large orange crystal region (about 10 mm × 6 mm × 2 mm). The crystal surface is bright, and the crystal surface and triangular crystal structure are clear. It is initially determined to be the 111-crystal surface of ZnTe. This location is in the final condensation area and is also corresponding to the highest temperature. The crystal region at the end of the ground sample is very small (about 3 mm × 3 mm × 1 mm). At the end of the stage, there is a small amount of orange ZnTe particles at the junction of the ingot and the plug, but there is no obvious, large crystal structure. They may be polycrystalline or non-crystals of ZnTe and Te. Therefore, the crystal size of the tail of the space sample is superior to that of the ground sample.

Fig. 4 Comparison of the tail sections of space and ground samples (a-space, b-ground)

图 4 空间样品和地面样品尾部照片(a) 空间,(b) 地面

In order to further analyze the uniformity of the distribution of Zn, Cu, and Te elements in the radial and axial compositional uniformity of the tail, the composition analysis was carried out by means of Scanning Electron Microscopy and Energy Dispersive Spectrum analysis. This test uses Zeiss ∑300 Field Emission Scanning Electron Microscope, field excitation voltage is 15 kV, magnification X 500 times, large field of view can be more accurate component distribution analysis. The energy spectrometer is EDAX. Figure 5 shows the analysis of the axial compositional uniformity of space sample and ground sample, while the red dot line in figure 5a is the space sample with better uniformity than the ground sample (figure 5a, black dot line). Figure 5a shows that ground sample levels of the Cu component vary significantly. Figure 5b shows the axial Te/Zn ratio of the space sample (red dot line) and the ground sample (black dot line), and the Te/Zn ratio of the ground sample is significantly higher than the Te/Zn ratio of the space sample, which shows that The component segregation and Te inclusion in the ground sample are more serious, while space microgravity growth helps to reduce the Te/Zn ratio.

Figure 6 shows the analysis of the radial compositional uniformity of the space sample and the ground sample, while the red dot line in figure 6a is a space sample with better uniformity than the ground sample (figure 6a, black dot line). In Figure 6a, the content of the Cu component in the ground sample is more volatile. Figure 6b shows the axial Te/Zn ratio of the space sample (red dot line) and the ground sample (black dot line). However, the Te/Zn ratio of the ground sample is also significantly higher than the Te/Zn ratio of the space sample, which shows that in the analysis of the radial compositional uniformity of the samples, the component segregation and Te inclusion in the ground sample are more serious, while space microgravity growth is helpful to reduce the Te/Zn ratio. However, it is also found that the radial Te/Zn ratio has a declining trend which needs a further analysis.

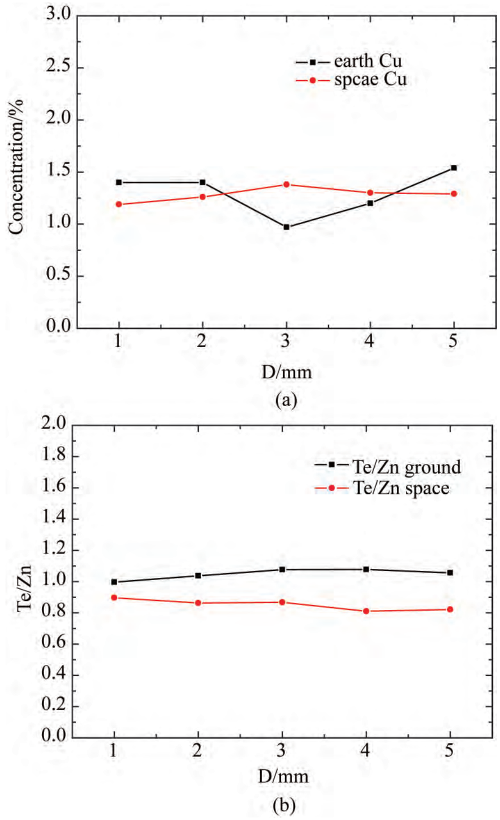

Fig. 5 Comparison of axial compositional uniformity distribution of space and ground samples

图 5 空间和地面样品横向组分分析

The analysis of axial and radial uniformity of Figures 5 and 6 shows that the axial uniformities of both space and ground samples are superior to the radial uniformities. The uniformity of Cu in space sample is better than that of ground sample, and the rich Te segregation of ground sample is more serious.

3 Conclusions

The Cu-doped ZnTe crystals were grown by Te solvent method under gravity and microgravity conditions. Cu was doped in the starting ingredients, and samples with the same parameters were grown on the ground. Space and ground samples were compared with Scanning Electron Microscopy and Energy Dispersive Spectrum analysis and X-ray CT scan.

Energy Dispersive Spectrum analysis shows that the uniformity of Te, Cu and Zn in space sample is better than that of ground sample, and the Te/Zn ratio is grea-

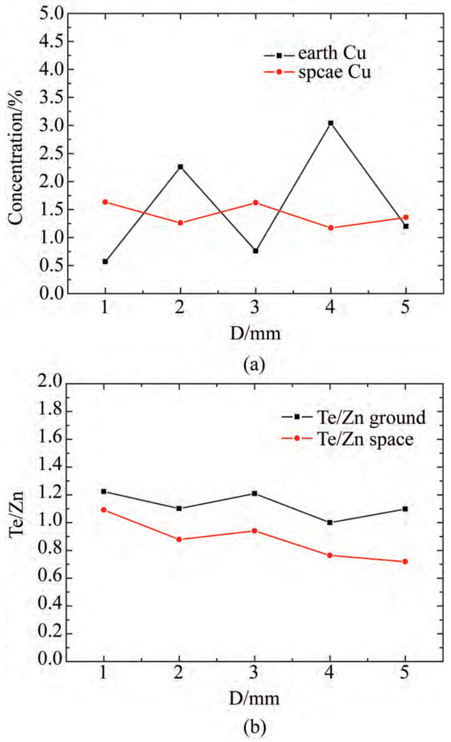

Fig. 6 Comparison of radial compositional uniformity distribution of space and ground samples
图6 空间和地面样品纵向组分分析

ter than 1, serious Te segregation in the ground sample indicates that the microgravity environment is effective to the reduction of Te inclusions.

The crystalline of space crystal are better than that of the ground crystals. The space sample with a size of 10 mm × 6 mm × 2 mm crystal in the final condensation area is larger than the ground sample with a size of 3 mm × 3 mm × 1 mm crystal. The results have shown that the microgravity condition is preferable to the growth of II–VI semiconductor materials.

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