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Production of Homogeneous $\text{Cu}_2\text{ZnSnS}_4$ by Splat Solidification in Microgravity

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Abstract

$\text{Cu}_2\text{ZnSnS}_4$ is used for chalcopyrite thin film solar cells with a high absorption coefficient and 1.5eV band-gap energy because elements of $\text{Cu}_2\text{ZnSnS}_4$ are non-toxic and abundant in the Earth's crust. High performance chalcopyrite thin film solar cells with homogeneous composition and structure are expected to be produced by laser ablation of $\text{Cu}_2\text{ZnSnS}_4$ bulk. In order to synthesize the homogeneous $\text{Cu}_2\text{ZnSnS}_4$ bulk, the $\text{Cu}_2\text{ZnSnS}_4$ melt was solidified by splat solidification using braking of a drop tower. For the ground-based experiments, the melt sample was pushed by pressurized Ar gas that had a force equal to that of deceleration force of the drop tower, and was blown against Cu chill block to solidify. The solidified sample had homogeneous composition and no grain boundary; in contrast, the samples that were solidified by pressurized Ar gas and air-cooled in normal gravity had heterogeneous composition and grain boundaries.

1. Introduction

Chalcopyrite type thin-film solar cells have high efficiency and a high absorption coefficient. So far, investigation has focused mainly on CuInSe_2 thin-film solar cells. However, 30 tons of In is necessary to generate 1GW of electricity using CuInSe_2 thin-films solar cells, according to Thumm *et al.*¹⁾ Moreover, there is little In in the Earth's crust, and a large amount of In is used as a transparent electrodes of liquid crystal displays. Also, the Se in CuInSe_2 is toxic. Other chalcopyrites that do not contain In and Se are expected to be developed. **Figure 1** illustrates a multi-element semiconductor system. CuInSe_2 can be changed to $\text{Cu}_2\text{ZnSnS}_4$. Zn and Sn are abundant in the Earth's crust, and S is non-toxic. Properties of $\text{Cu}_2\text{ZnSnS}_4$ as a semiconductor are expected to be the same as those of CuInSe_2 , as indicated by the crystalline structures depicted in **Fig. 2**. In fact, $\text{Cu}_2\text{ZnSnS}_4$ has 1.5eV band-gap energy that is

suitable for solar cells and a high absorption efficiency of more than 10^4cm^{-1} ²⁾.

In 1988, Ito *et al.* studied electrical and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ that was synthesized by atom beam sputtering.²⁾ In 1996, they prepared $\text{Cu}_2\text{ZnSnS}_4$ thin films by solution spraying.³⁾ In 2007, Jimbo *et al.* synthesized $\text{Cu}_2\text{ZnSnS}_4$ thin-film solar cells with a maximum efficiency of 5.74% by radio frequency (rf) magnetron co-sputtering.⁴⁾ In 2008, Scragg *et al.* annealed $\text{Cu}_2\text{ZnSnS}_4$ electrodeposition films to improve their quality.⁵⁾

To obtain high-frequency thin-film solar cells, the film should have homogeneous composition and no grain boundaries. It is difficult to prepare $\text{Cu}_2\text{ZnSnS}_4$ thin-films with homogeneous chemical composition and no grain boundaries by multi-source elemental evaporation because the sputtering efficiency is different for each element. Also, sulfurization of the

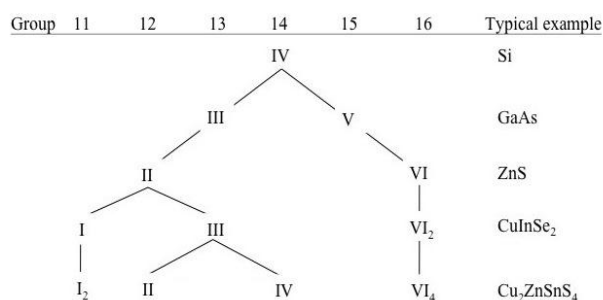


Fig.1 Multi-elements Semiconductors.

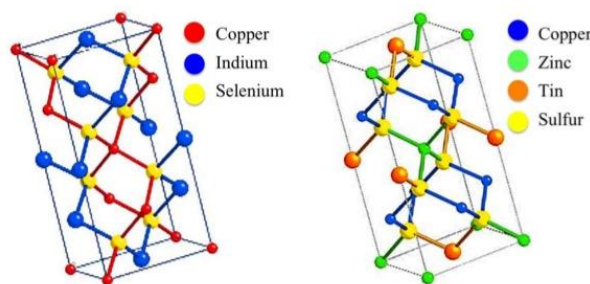


Fig.2 Structure of CuInSe_2 (left) and $\text{Cu}_2\text{ZnSnS}_4$ (right).

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film's metals synthesizes not only $\text{Cu}_2\text{ZnSnS}_4$ but also other metal sulfides. However, it is thought that laser ablation can prepare thin film with homogeneous composition and no grain boundaries by using a target with homogeneous composition and no grain boundaries. However, the synthesis of $\text{Cu}_2\text{ZnSnS}_4$ thin film by laser ablation using a homogeneous target has not yet been reported.

Splat-solidification of 2Cu-Zn-Sn-4S melts is thought to be able to synthesize the target for laser ablation with homogeneous composition and no grain boundaries. However, splat solidification cannot synthesize products with homogeneous composition and no grain boundaries in some cases, depending on the properties of melts, such as aggregations of the same components in the melt. With $\text{Cu}_2\text{ZnSnS}_4$, the ZnS primary crystal is formed in the first stage of solidification, and then ZnS reacts with Cu-Sn-S melt to form $\text{Cu}_2\text{ZnSnS}_4$. The ZnS nuclei collide with each other to make ZnS grains. The peritectic reaction of ZnS grain with Cu-Sn-S melts is slow, and unreacted ZnS grains are detected in the splat-solidified product. In microgravity (μg), ZnS nuclei do not collide because there is no convection in the melt. The ZnS nuclei that are kept in μg easily react with Cu-Sn-S melt to form $\text{Cu}_2\text{ZnSnS}_4$. $\text{Cu}_2\text{ZnSnS}_4$ with homogeneous composition and no grain boundaries is thought to be synthesized by splat solidification in μg .

In this study, we investigate the synthesis of $\text{Cu}_2\text{ZnSnS}_4$ with homogeneous composition and no grain boundaries by splat solidification in short-time μg .

2. Experimental

2.1 Samples

Cu (99.5% purity), Zn (99.0% purity), Sn (99.5% purity) and S (99.0% purity) powders (Wako Pure Chemical Industries, Ltd.) were used in this study. The metal powders of Cu, Zn, and

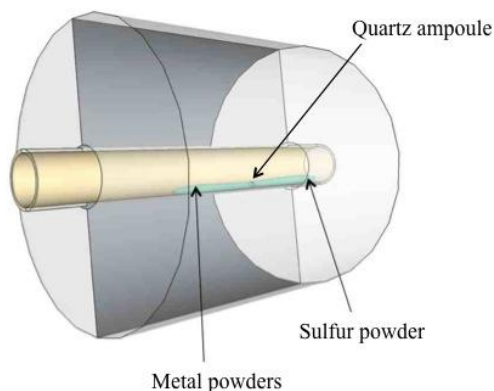


Fig.3 Schematic diagram of apparatus for sulfurization of metal powders.

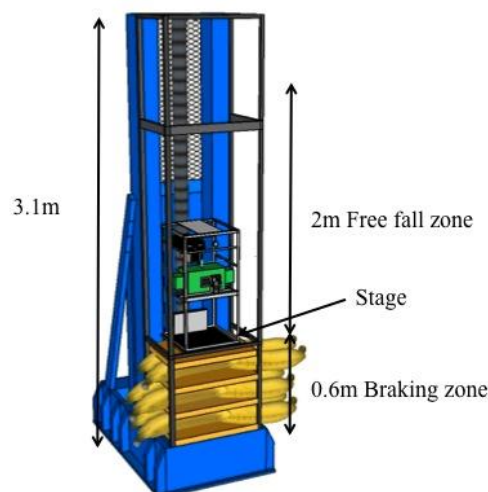


Fig. 4 the 2m-drop tower.

Sn with 2:1:1 atomic ratio and S equivalent for metals were placed in an 8mm diameter, 20cm long quartz ampoule vacuumed to $1.3 \times 10^{-1}\text{Pa}$. The metal powders were placed at one end of the ampoule and S powder was placed at the other end. The ampoule was set in an electric resistance furnace (**Fig. 3**).

The metal powders were heated at 1100K, and S was heated at 700K for 24 hours for the metals to react metals with S. The sample was then heated at 1273K for 3 hours to homogenize it (the melting point of $\text{Cu}_2\text{ZnSnS}_4$ is 1253K.⁶⁾), and $\text{Cu}_2\text{ZnSnS}_4$ samples were obtained. The heating and cooling rate of the samples was 2K/min.

2.2 Splat Solidification in μg

We carried out splat solidification experiments in μg using a 2m drop tower (**Fig. 4**). This tower is composed of a 2.0m free-fall zone and a 0.6m braking zone to obtain μg of 10^{-2}g for 0.46s. A 250kg apparatus 450mm long x 450mm wide x 850mm high is set on the stage of the drop tower, and the apparatus and stage freely fall for 2m. **Figure 5** indicates the μg level of 10^{-2}g for 0.46s in the free fall zone and 3.2g for the braking zone. After the apparatus falls 10cm from the top of the drop tower, the electric power of the IR (infrared) furnace is turned off to stop heating. Bead cushions (particle size of 1mm) and urethane foam mattresses are used to decelerate the apparatus.

The splat solidification apparatus (**Fig. 6**) was composed of an IR furnace (Shinku-riko: MR-39D), a sequence timer for the drop signal and turning the furnace on and off, a temperature controller for the furnace, a video camera, and a pressure gauge. The sample was loaded in a carbon crucible in a reactor tube. This crucible had 1mm diameter nozzle at one end. The tube was set in the furnace, and the atmosphere in the tube was set to S of 0.1MPa. The apparatus was placed on the stage set on the

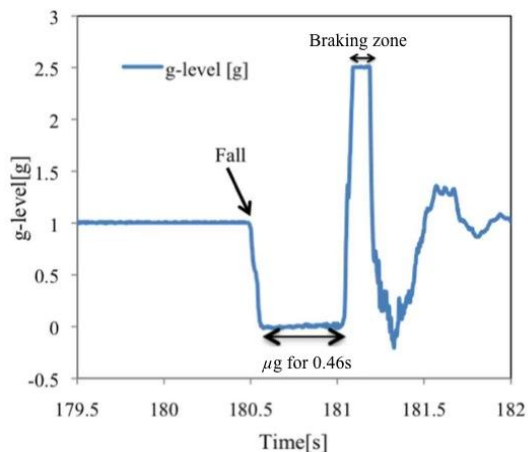


Fig. 5. μg level of the tower.

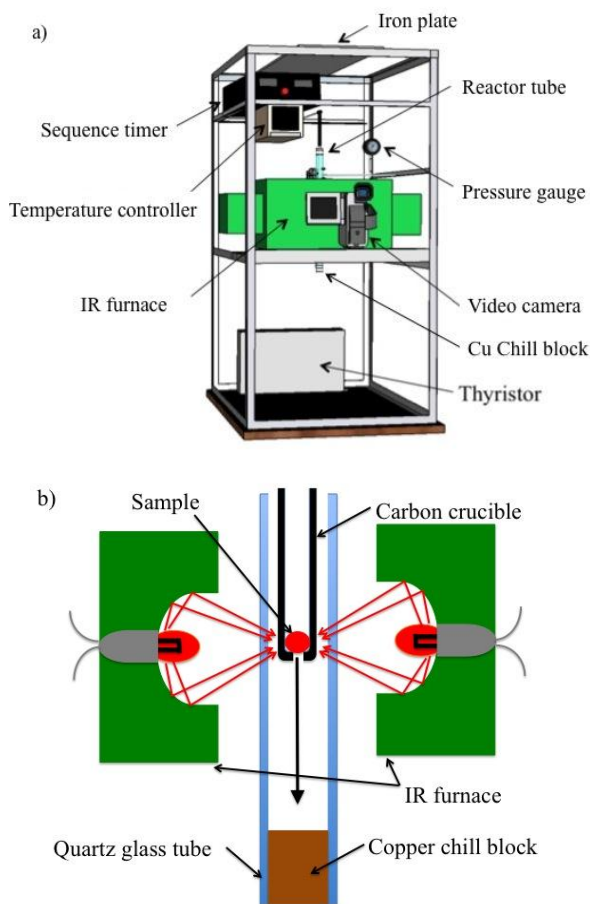


Fig. 6. Apparatus of sput-splattification (a: appearance, b: sput-splattification system).

top of the drop tower. The sample was heated to 1450K for 3min by the IR furnace to melt completely. The apparatus was then dropped, and the melted sample was subjected to microgravity, and then dropped from nozzle when the apparatus was braked. The cooling rate of the splat solidification is so rapid (over 10^4 K/s) that the molten droplet was solidified before it was affected by braking. Therefore, the molten droplet wasn't influenced by braking. The molten droplet struck on the

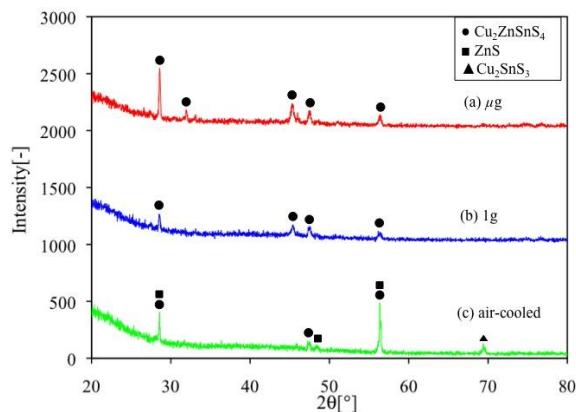


Fig.7 XRD patterns of the section surface parallel to the cooling direction of the samples splat-solidified in μg (a) and 1g (b), and section surface of air-cooled sample (c).

Cu chill block. For the ground-based experiments, the sample was pushed by 0.32MPa Ar gas, which is equal to the braking force of the drop tower. The melt then impacted on the chill block where it solidified.

The solidified samples were embedded in epoxy resin, and the section surfaces of the samples were polished and etched for 30 sec by nital solution (95vol% ethanol and 5vol% nitric acid) for analysis by SEM (Scanning Electron Microscope, JSM-5200, JEOL), EDX (Energy Dispersive X-ray Spectroscopy, JSM-6390 and JED-2300, JEOL), and XRD (X-ray Diffractometer, RINT2000/PC, RIGAKU).

3. Results

3.1 Crystalline Compounds of Splat-Solidified Products

Figure 7 plots XRD patterns of μg and 1g splat-solidified and air-cooled samples. The air-cooled sample contained ZnS and Cu_2SnS_3 . However, the samples splat-solidified in μg and 1g contained only Cu_2ZnSnS_4 single phase.

3.2 Structure of splat-solidified products

Figure 8 presents SEM images of the section surface parallel to the cooling direction of samples splat solidified in μg and 1g, and the section surface of the air-cooled sample. Here, (a) and (c) depict the section surface near the surface of the sample splat solidified in μg and 1g contacting the Cu chill block. (b) and (d) depict the section surface near the free surface of the sample splat-solidified in μg and 1g, and (e) depicts the section surface of air-cooled sample. The section surface of (a) exhibited homogeneous composition, and the crystalline phase was only Cu_2ZnSnS_4 , based on the result of XRD (Fig.7). Other section surfaces had heterogeneous composition with many grains.

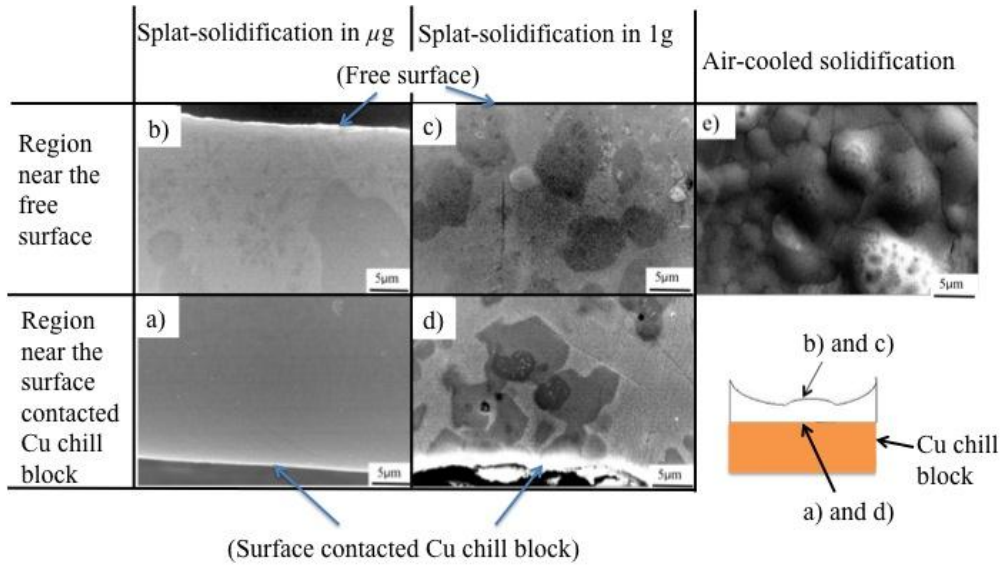


Fig. 8. SEM images of section surface parallel to the cooling direction of samples splat-solidified in μg and 1g , and section surface of air-cooled sample.

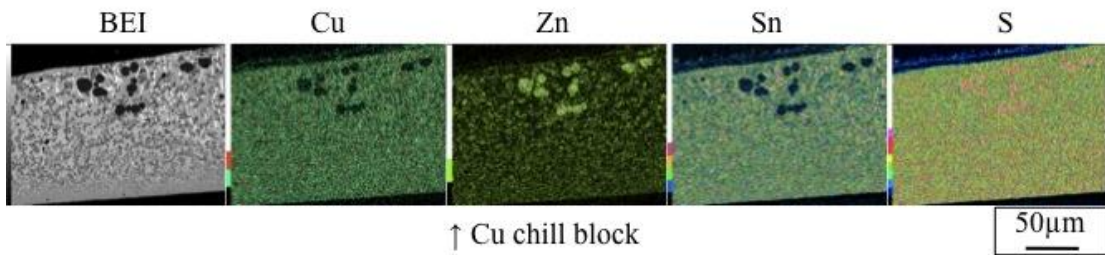


Fig. 9. Backscattered electron image (BEI) and element distributions of Cu, Zn, Sn and S of section surface parallel to the cooling direction of sample splat-solidified in μg .

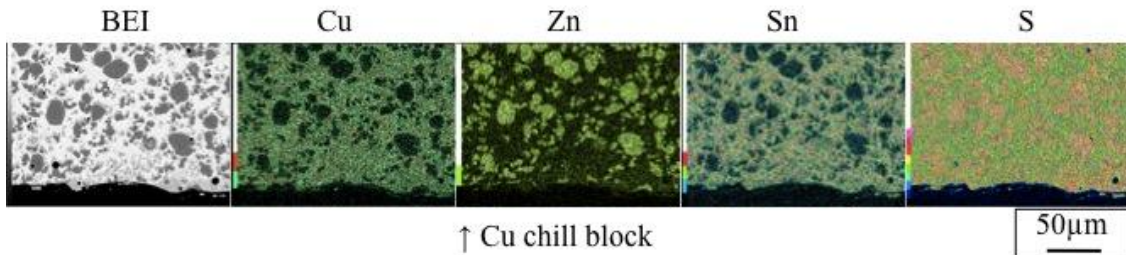


Fig. 10. Backscattered electron image (BEI) and element distributions of Cu, Zn, Sn and S of section surface parallel to the cooling direction of sample splat-solidified in 1g .

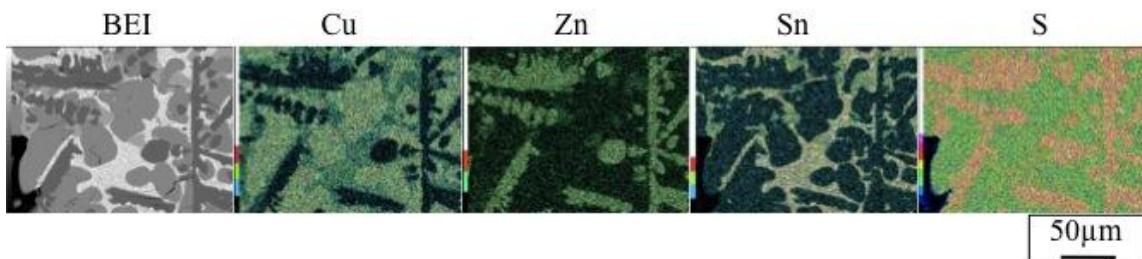


Fig. 11. Backscattered electron image (BEI) and element distributions of Cu, Zn, Sn and S of section surface of air-cooled sample.

3.3 Element Distributions in Splat-Solidified Products

Figures 9, 10, and 11 illustrate the distribution of Cu, Zn, Sn, and S of the section surface parallel to the cooling direction surface splat-solidified in μg and 1g, and the section surface of the air-cooled solidified sample. The sample splat-solidified in 1g and the air-cooled sample exhibited grain boundaries (Figs. 10 and 11). However, the sample splat-solidified in μg was homogeneous, with no grain boundaries in the region $75\mu\text{m}$ from the surface that contacted the Cu chill block (Fig.9).

4. Discussion

$\text{Cu}_2\text{ZnSnS}_4$ was produced by the peritectic reaction of $\text{Cu}_2\text{SnS}_3\text{-ZnS}^{(6)}$ as indicated in the quasi-binary phase diagram presented in Fig. 12. The results of EDX indicated that the sample splat-solidified in 1g had grains of Cu-Sn-S and Zn-S (Fig.10), though XRD results indicated single-phase $\text{Cu}_2\text{ZnSnS}_4$. The air-cooled sample had grains of Cu-Sn-S (Cu_2SnS_3) and Zn-S (ZnS), according to the results of XRD and EDX. In contrast, the sample that was splat-solidified in μg was homogeneous, with no grain boundaries in the region $75\mu\text{m}$ from the surface that contacted the Cu chill block, and it has only $\text{Cu}_2\text{ZnSnS}_4$ phase. The melt that is mixed by thermal convection in 1g can be maintained in a homogeneous state in μg . When the homogeneous melt was cooled in μg , the primary crystal, ZnS, was very fine and, following peritectic reaction, easily and rapidly changes to $\text{Cu}_2\text{ZnSnS}_4$. The process from ZnS to $\text{Cu}_2\text{ZnSnS}_4$ proceeds quickly by splat solidification in μg .

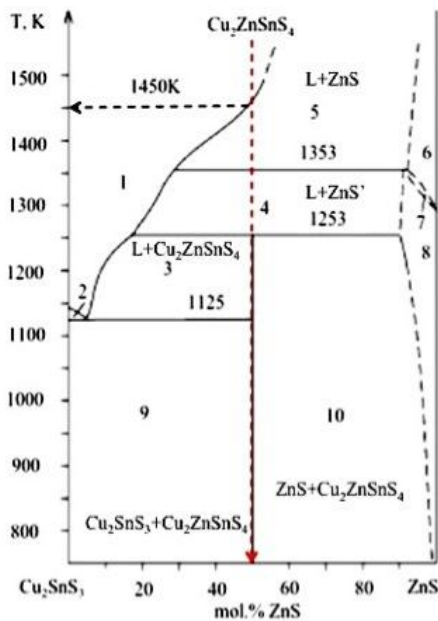


Fig. 12. Quasi-binary phase diagram of $\text{Cu}_2\text{SnS}_3\text{-ZnS}$.
 (1)L (2) $\text{L}+\text{Cu}_2\text{SnS}_3$ (3) $\text{L}+\text{Cu}_2\text{ZnSnS}_4$ (4) $\text{L}+\text{ZnS}'$ (5) $\text{L}+\text{ZnS}$ (6) ZnS (7) $\text{ZnS}+\text{ZnS}'$
 (8) ZnS' (9) $\text{Cu}_2\text{SnS}_3+\text{Cu}_2\text{ZnSnS}_4$ (10) $\text{ZnS}'+\text{Cu}_2\text{ZnSnS}_4$
 * ZnS' is the solid solution range of the low-temperature modification of ZnS.

Fig. 12. Quasi-binary phase diagram of $\text{Cu}_2\text{SnS}_3\text{-ZnS}$.

Therefore, homogeneous single-phase $\text{Cu}_2\text{ZnSnS}_4$ was formed from splat solidification in μg . However, homogeneous melt is obtained in 1g because of mixing by thermal convection, and the melt is always moving at a temperature above the melting point. When the melt was cooled, the primary crystals collide with each other and cohere from nuclei to grains. The peritectic reaction to $\text{Cu}_2\text{ZnSnS}_4$ from ZnS particle was not completed during splat solidification to form heterogeneous products.

The temperature profile of splat solidification was estimated using the model depicted in Fig. 13. The model was applied to Fourier's law (equation 1),

$$-k_s A \frac{T_2 - T_1}{\Delta x_2} = -k_{Cu} A \frac{T_3 - T_2}{\Delta x_1} \quad (1)$$

where k is thermal conductivity and A is area. Table 1 presents the parameters of the equation. When the melt was solidified at the peritectic point (1125K), the solidification thickness was estimated to be $31\mu\text{m}$. The thickness of the finely homogeneous region is the same as that of the finely homogeneous region depicted in Fig.9, and the region was thought to solidify from the temperature of the appearance of primary crystals to the peritectic point. A coarsely homogeneous region $45\mu\text{m}$ thick in the finely homogeneous region existed in the sample splat-solidified in μg . This region was thought to solidify at temperature from the peritectic point to the end of μg . The $50\mu\text{m}$ -thick heterogeneous region on the coarsely homogeneous region was thought to solidify in 1g. The homogeneous region of $\text{Cu}_2\text{ZnSnS}_4$ can be used as the target of laser ablation.

Table 1. The parameter for the solidification model.

Temperature	T_1 : 1253K ⁽⁶⁾ , T_2 : 1125K, T_3 : 293K
Thermal conductivity	k_s : 3.8W/(m K) ⁽⁷⁾ , k_{Cu} : 394W/(m K)
Area	A : $1.76 \times 10^{-4} \text{m}^2$ Δx_1 : 0.02m

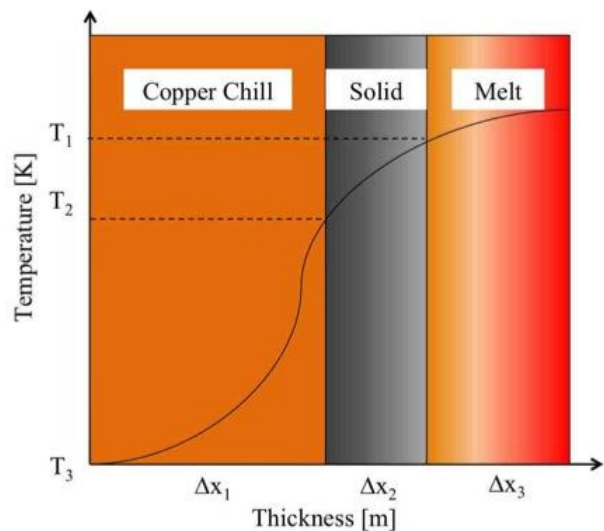


Fig. 13. Temperature profile during splat-solidification heated 2Cu-Zn-Sn-4S melt on the Cu chill block.

4. Conclusion

The splat-solidification of 2Cu-Zn-Sn-4S melt in μg resulted in Cu₂ZnSnS₄ with a homogeneous composition and no grain boundaries. This Cu₂ZnSnS₄ was formed by splat solidification with rapid cooling of the melt without convection in μg . The Cu₂ZnSnS₄ with the homogeneous single phase and no grain boundaries can be used as a target of laser ablation to prepare high-quality thin Cu₂ZnSnS₄ film for solar cells.

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