Growth and Characterization of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ Single Crystal Grown by Traveling Heater Method

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Abstract

High-quality $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ ($\text{CZTS}_x\text{Se}_{1-x}$) single crystals were grown by the traveling heater method (THM), which is an example of a solution growth process. The $\text{CZTS}_x\text{Se}_{1-x}$ solute – Sn solvent pseudobinary system was investigated and the ranges of growth temperature and quantity of solvent determined for THM growth. The $\text{CZTS}_x\text{Se}_{1-x}$ single crystals were obtained from a 70~80 mol% $\text{CZTS}_x\text{Se}_{1-x}$ solution at growth temperature 900°C and speed 4~5 mm/day. The structural and compositional analyses of the grown single crystals were carried out by powder X-ray diffraction, Raman spectroscopy and electron probe microanalysis. The grown crystals were kesterite and nearly stoichiometric with slightly Cu-poor and Zn-rich despite the excess Sn used as the solvent. As the sulphur content x increases, the carrier concentration increases slightly but systematically between 2 to $3 \times 10^{17} \text{ cm}^{-3}$ while the mobility decreases from 35.1 to $10.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. These data provide references for the results of characterization on thin film samples as well as giving insight into the defect equilibrium and resulting quantities such as doping and mobility affecting device performance.

Keywords : B1. $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe), B2. Quarternary compounds, A2. Growth from solutions, A2. Traveling solvent zone growth

1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ ($\text{CZTS}_x\text{Se}_{1-x}$) are being extensively researched as absorbing layer materials for low nontoxic and earth abundant thin film solar cell devices because of their possible reduced constraints to scale up because of greater material availability and well-suited great physical properties such as a direct bandgap structure and a high absorption coefficient [1, 2]. Recently, a power conversion efficiency of 12.6% was achieved for $\text{CZTS}_x\text{Se}_{1-x}$ solar cell using a hydrazine assisted deposition approach [3]. The efficiency of $\text{CZTS}_x\text{Se}_{1-x}$ devices have been continuously improved from 6.7 % (2008) [4] to 9.7 % (2010) [5] and 11.1 % (2012) [6]. These results indicate the substantial promise of this new photovoltaic materials system, however there is room for improvement.

The open circuit voltage is low value compared to the bandgap energy [3-6]. An adequate reason is it is difficult to control the effective bandgap energy because of inhomogeneities in composition and crystal phase. For example, CZTS have disorder of Cu and Zn in the crystal structures which are kesterite or stannite structures. The stable energy difference between the kesterite and stannite structure is only approximately 3 meV per atom, and the bandgap energy of kesterite structure is 0.12 eV higher than that of stannite in CZTS [7]. Scragg *et al.* reported the transition between ordered and disordered CZTS at critical temperature of 533 K using Raman scattering measurement [8]. On the other hand, all kesterite solar cells with reported efficiencies higher than 8% indicates non-stoichiometric composition, which is Cu-poor and Zn-rich condition [3, 9, 10]. Intuitively, this suggests a high population of intrinsic defects and the possible co-existence of a secondary phase such as ZnS. From first-principles calculations, it has been shown that the Cu on Zn antisite (Cu_{Zn}) and the Cu vacancy (V_{Cu}) are the dominant acceptor defects in CZTS, which leads to p-type conductivity [2].

Inhomogeneities such as grain boundaries, twins, dislocations, antiphase domains, as well as second phases all may be present in kesterite thin films and may directly affect the power conversion efficiency. It is important to grow high-quality $\text{CZTS}_x\text{Se}_{1-x}$ single crystal in order to investigate the above phenomena. In our previous crystal growth studies, high-quality CZTS single crystals were obtained by the traveling heater method (THM), which is an example of a solution growth process [11, 12]. It is generally difficult to grow high-quality single crystals of the $\text{I}_2\text{-II-IV-VI}_4$ compounds from a melt, because most of the compounds grow through a peritectic reaction or a solid state transition during the cooling process [13, 14]. CZTS and CZTSe are formed according to the peritectic reaction (liquid phase + ZnS or ZnSe), therefore THM growth, which can proceed below the melting point, is well suited to the growth of high-quality $\text{CZTS}_x\text{Se}_{1-x}$ single crystals. Furthermore, we have already obtained feed polycrystalline $\text{CZTS}_x\text{Se}_{1-x}$ for THM by using melt growth [15]. In our previous electrical and optical studies using high-quality CZTS single crystal samples, CZTS exhibits defect-mediated transport (hopping conduction) at low temperature, a conductivity activation energy of 130 meV for higher temperatures and the large-density band tail states formed below the band edge [16, 17].

In this study, we have investigated the growth of high quality mixed $\text{CZTS}_x\text{Se}_{1-x}$ crystals using THM with Sn as solvent. Therefore, we examine the phase equilibria between the solid and liquid phases in the $\text{CZTS}_x\text{Se}_{1-x}$ - Sn pseudobinary system in order to obtain useful understandings for THM growth.

2. Experimental procedure

2.1 CZTS_xSe_{1-x}-Sn pseudobinary system

For each composition of CZTS_xSe_{1-x}, polycrystalline source material was grown by a melt growth method. Stoichiometric ratios of Cu (5N), Zn (6N), Sn (6N), S (6N), and Se (5N) according to Cu₂ZnSn(S,Se)₄ were charged into a carbon-coated quartz ampoule with a 10 mm diameter. The ampoule, charged with the elements, was sealed off after evacuation to a pressure of 10⁻⁶ Torr. Then the ampoule was inserted into a vertical furnace, heated up to 1100 °C with 100 °C /h, and kept at this temperature for 24 h. After keeping 1100 °C for 24h, the ampoule was cooled in the atmosphere [15].

In this paper, when discussing the Sn- CZTS_xSe_{1-x} pseudo binary system, X is defined as the mol% of the CZTS_xSe_{1-x} solute in the Sn solution:

$$X [\text{mol}\%] = \frac{\text{CZTSSe} [\text{mol}]}{\text{CZTSSe} [\text{mol}] + \text{Sn} [\text{mol}]} \times 100. \quad (1)$$

Polycrystalline CZTS_xSe_{1-x} and Sn in the prescribed ratio of X were inserted into a quartz ampoule with a 10 mm diameter. The CZTS_xSe_{1-x} solute ingots weighed approximately 10 g, and the required weight of the Sn solvent was calculated from Eq. (1). Then a mixture of CZTS_xSe_{1-x} and Sn was sealed in a quartz ampoule under a high vacuum of ~ 10⁻⁶ Torr, and synthesized homogeneously by heating 1100 °C at a rate of 200 °C /h for 48 h. The ampoule was then pulled out from the vertical furnace and quenched in the water. The liquidus temperature for each sample was investigated by differential thermal analysis (DTA) and by visually observation. For DTA measurement, the mixtures were weighed to about 10~20 mg and sealed in a quartz ampoule with a 3.5 mm diameter under a high vacuum of ~ 10⁻⁶ Torr. Al₂O₃ was used as a reference material. DTA temperature was calibrated by the melting point of Zn, Sn and In. Heating and cooling rates were 10 °C /min with an accuracy of ± 1 °C. The sample and reference temperature was determined with 13%RhPt-Pt thermocouples. For each peak in the difference signal, a phase transition temperature was determined from the

extrapolated onset of DTA peaks in the heating and cooling process. The temperature of the liquid was also visually observed during a cycle of slow heating and cooling in a transparent furnace. The accuracy of the temperature was ± 10 °C. In order to identify the phases in equilibrium along the liquidus curve which were observed visually, a $\text{CZTS}_x\text{Se}_{1-x}$ -Sn synthesized ingot prepared as above was heated to the determined liquidus point at a rate of 200°C/h in a vertical furnace. After keeping for 48 h, the ampoule was pulled out from the vertical furnace and quenched in water. Cross sections were cut from the synthesized ingot, from which the phases were inspected. The phase and composition were determined by the powder X-ray diffraction (XRD) and electron probe microanalysis (EPMA), respectively.

2. 2 Growth and characterization of $\text{CZTS}_x\text{Se}_{1-x}$ single crystal

The $\text{CZTS}_x\text{Se}_{1-x}$ single crystal was grown from Sn solution. A polycrystalline $\text{CZTS}_x\text{Se}_{1-x}$ feed ingot and Sn solvent were loaded into a carbon-coated quartz ampoule with a diameter of 10 mm. The ampoule was sealed under high vacuum (10^{-6} Torr), then inserted into the THM furnace. Growth of the $\text{CZTS}_x\text{Se}_{1-x}$ single crystal was performed by pulling the ampoule through the THM furnace. The THM growth principle was described in our previous report [11, 12]. The $\text{CZTS}_x\text{Se}_{1-x}$ single crystal structure was examined by powder XRD and Raman spectroscopy. The orientation and crystallinity of $\text{CZTS}_x\text{Se}_{1-x}$ single crystal were investigated by the X-ray rocking curve (XRC) method. Cu- K_α radiation was used for the powder XRD as XRC measurements. A tube voltage for XRD, a tube current and step width were 40 kV, 40 mA and 0.01 deg, whereas 45 kV, 40 mA and 0.002 ° were used for XRC. A 514 nm Ar ion laser was used in the Raman measurements and focused on the sample by an objective lens with a numerical aperture of 0.55. The power of the incident laser was 100 mW on the sample. The spectra were calibrated by a Si peak position of 520 cm^{-1} . The composition of the $\text{CZTS}_x\text{Se}_{1-x}$ single crystals was determined by EPMA. The electrical properties were determined by using

resistivity and Hall effect measurements. Hall measurements were carried out at room temperature under 0.54 T magnetic field in the Van der Pauw geometry. The sample dimensions were $5\text{ mm} \times 5\text{ mm} \times 0.5\text{ mm}$ and the sample was mechanically polished with $0.01\text{ }\mu\text{m}$ Al_2O_3 powder. Multiple Au contacts of diameter 1 mm were deposited by evaporation onto each $\text{CZTS}_x\text{Se}_{1-x}$ bulk single crystal to a thickness of 200 nm.

3. Results and discussion

3. 1. Phase diagrams of $\text{CZTS}_x\text{Se}_{1-x}$ - Sn system

Firstly, we investigated liquidus point of each composition by DTA measurement and visually observation, which are important understandings on solution growth. Figure 1 shows the DTA curves of $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0.5$) in the (a) heating and (b) cooling processes. The solid-liquid phase transition point was extrapolated from onset temperature of each process. In addition, we confirmed liquidus temperature by direct visually observation in order to compare to DTA results. Table 1 indicated the liquidus temperatures determined by each measurement technique. It is clear that good agreement is obtained.

The phases present for in the resulting ingots for each composition were determined by using XRD and EPMA measurements. The pictures of synthesized ingots cross section and phases composition are shown in Fig. 2 ($X= 10, 50$ and $90\text{ mol}\%$) and Table 2, respectively. The two phase separation at $10\text{ mol}\%$ was observed from visually and composition results. Phase 1 (L1 phase) is located at the bottom of the ampoule and is nearly pure Sn. This is because the Sn density [18] is higher than CZTSSe (for example, CZTS single crystal in this work = $4.404\text{ g}\cdot\text{cm}^{-3}$). On the other hand, phase 2 (L2 phase) is composed of $\text{CZTS}_{0.5}\text{Se}_{0.5}$ solute and Sn solution. The powder XRD patterns of $X= 50$ and $90\text{ mol}\%$ are shown in Fig. 3, which indicates the existence of phase separation visually. The pattern of $X= 50\text{ mol}\%$ (phase 3) in the two phase region includes peaks from a $\text{Sn}(\text{S}, \text{Se})_x$ secondary phases. The phase 4 region at $X= 90$

mol% is composed of the peaks from a CZTSSe compound and Sn solvent. No phase separation was observed at Sn solutions with $X > 60$ mol%. In this region, CZTS_{0.5}Se_{0.5} solute dissolve Sn solvent, typically.

On the basis of above data, we have constructed the pseudobinary phase diagram of CZTSSe-Sn system as shown in Fig. 4. It is impossible to grow CZTS_xSe_{1-x} single crystal at $X < 60$ mol%, because secondary phases were located at bottom of ampoules. Whereas Sn solutions with more than 60 mol% CZTSSe solutes was single phase. From the phase diagram, it was possible to grow CZTS_xSe_{1-x} single crystals at $X > 60$ mol% and 720 ~ 980°C.

3. 2. Growth and characterization of CZTS_xSe_{1-x} single crystal

3. 2. 1 THM growth results

Single crystal growth of CZTSSe was performed from Sn solution, based on the phase diagram determined. The each composition bulk single crystals were grown from a Sn solution of $X = 70$ -80 mol%. The growth temperature and speed were 900 °C and 4~5 mm/day. The temperature gradient at the point of growth was about tens of degrees per centimeter. A photograph of a CZTS_{0.5}Se_{0.5} single crystal cross section is shown in Fig. 5. The CZTS_{0.5}Se_{0.5} single crystal is approximately 10 mm in diameter and 25 mm in length, the end portion is the remaining Sn solvent zone. No grain boundary was observed, and the Laue back-reflection pattern, which is shown in our previous CZTS single crystal study, was also observed for this sample [11].

3. 2. 2 Structural properties

Figure 6 shows the XRC for (112) oriented CZTS_{0.5}Se_{0.5} single crystal. The obtained CZTSe crystallinity is good because the value of full-width at half-maximum (FWHM) is 165 arcsec, which is similar value to CZTSe single crystal in our previous studies [19]. The values of FWHM for all samples indicate between 100 ~ 165 arcsec.

Figure 7 shows the powder XRD pattern of the each composition $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.2, 0.5, 0.8$ and 1.0) single crystal. It is very difficult to investigate the CZTSSe single phase from XRD measurement because the peaks of CZTSe overlap well with those of $\text{Cu}_2(\text{S}, \text{Se})$ and $\text{Zn}(\text{S}, \text{Se})$, especially. Therefore, we have also investigated CZTSSe single phase by the Raman spectroscopy. The XRD pattern of all samples exhibit major peaks corresponding to diffraction lines of the Kesterite structure of CZTSSe (ICDD data #00-026-0575 CZTS and #00-052-0868 CZTSe). No other peaks of secondary phases are observed in the XRD pattern. The diffraction peaks from (112), (204) and (312) planes were observed clearly in all samples indicating the formation of CZTSSe phase. In our previous studies [12, 19], the lattice constants of a - and c -axes in CZTS and CZTSe were calculated from the XRD patterns. Their constants were estimated for CZTS, $a = 5.443 \text{ \AA}$ and $c = 10.879 \text{ \AA}$ whereas for CZTSe, $a = 5.692 \text{ \AA}$, $c = 11.434 \text{ \AA}$. Those of CZTSSe samples also were calculated and clearly proportional to the increasing of S composition values x , indicating that they follow Vegard's law.

Moreover, we could not observe any differences by the Raman spectroscopy shown in Fig. 8. The Raman spectroscopy is useful to investigate the structure and phase purity of multinary compounds such as $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.2, 0.5, 0.8$ and 1.0) samples besides XRD measurement. The spectra show clear the peaks of CZTS at $287, 338$ and 371 cm^{-1} , while that of CZTSe at $170, 193$ and 230 cm^{-1} in our previous studies [12, 19]. No major peaks of the secondary phases were observed in the spectra. $\text{Cu}_2\text{Sn}(\text{S}, \text{Se})_3$ have tetragonal or cubic structure with very similar lattice constants to CZTSSe. The peaks of tetragonal Cu_2SnS_3 are present at $336\text{-}337 \text{ cm}^{-1}$, which correspond to CZTS A_1 mode peak, however other distinct peaks are not observed at $303, 355 \text{ cm}^{-1}$ (cubic) and 351 cm^{-1} (tetragonal) [20]. The ZnS peaks which would be at $218, 295, 386, 422$, and 448 cm^{-1} are not observed [21]. In addition, other possible secondary phases, for example Cu-S compounds and Sn-S compounds, are also not observed [22]. The peaks of Cu_2Se 263 cm^{-1} , ZnSe 205 cm^{-1} and 251 cm^{-1} , SnSe_2 186 cm^{-1} and Cu_2SnSe_3 are also not

observed [23-26]. The strongest peaks at 337 cm^{-1} in CZTS and 192 cm^{-1} in CZTSe spectra are attributed to the A_1 symmetry which originates from the vibration of S or Se atoms surrounded by the motionless neighbouring atoms [27]. This mode is expected to correspond to the dominant peak in the Raman spectrum of CZTSSe. The spectra of CZTSSe single crystals with S composition values ($x = 0.2, 0.5$ and 0.8) indicated the peaks of two A_1 mode because of the co-existence of S and Se atoms in samples. These two modes clearly shift toward the high frequency region to being proportional to the increasing of S composition values x .

3. 2. 3 Compositional properties

The composition analysis results by EPMA measurement are shown in Table 3. The uncertainty in the compositions is less than 1%. The sample wafers were cut from the growth tip portion at 5 mm intervals except for the end region. The measurement points were three positions (edge and centre) of wafer. It was found that the compositions of $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.2, 0.5, 0.8$ and 1.0) single crystals were homogeneous in the wafers and along the growth direction and slightly Cu-poor and Zn-rich conditions, which is high performance composition in CZTSSe solar cell.

The observed phases in the pseudobinary $\text{CZTS}_x\text{Se}_{1-x} - \text{Sn}$ system by using Raman spectroscopy and powder XRD measurements include $\text{CZTS}_x\text{Se}_{1-x}$, liquid with a high proportion of Sn, $\text{Sn}(\text{S}, \text{Se})_x$. These phases are not all contained exclusively on either the $\text{Cu}(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})$ pseudo-ternary or $\text{Cu}_2(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})_2$ pseudo-ternary systems. Figure 9 (a) shows these two possible pseudo-ternary systems as green ($\text{Cu}(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})$ system) and blue ($\text{Cu}_2(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})_2$ system) planes within the quaternary Cu-Zn-Sn-S (Se) phase diagram. The former maintains a constant ratio of metal and S, while the latter maintains the formal oxidation states of the metals in the kesterite structure. They intersect along the $\text{Cu}_2\text{Sn}(\text{S}, \text{Se})_3 - \text{CZTSSe} - \text{Zn}(\text{S}, \text{Se})$ tie line.

The blue dashed line means the process of CZTSSe crystal growth from Sn solution. The phase compositions that occur do not all fall on exclusively one of these planes because solution growth is one of the non-equilibrium route. In fact, Du *et al.* and Lund *et al.* reported the investigation of combinatorial coevaporated thin film CZTS which is accompanying study each other [28, 29]. The observed phases under different growth condition such as variation of growth temperature and composition were explained by using CuS – ZnS – SnS pseudo-ternary and Cu₂S – ZnS – SnS₂ systems. We select to use the Cu₂S – ZnS – SnS₂ systems because this system is appropriate for synthesis routes based on fixed compositions such as growth in the quartz ampoules, which is similar to this study. Figure 9 (b) displays compositions of CZTSSe single crystal on Cu₂(S, Se) – Zn(S, Se) – Sn(S, Se)₂ systems. The Cu₂Sn(S, Se)₃ – CZTSSe – Zn(S, Se) tie line is characterized by the ratio Cu/Sn = 2. These grown crystals possess Cu-poor, Zn-rich and Sn-poor condition even though using excess Sn solvent, which are also observed at Cu/Sn > 2 region in Refs. 28 and 29. In addition, Feed polycrystalline in this study also possess same condition grown from stoichiometric ratio of each elements [15]. Therefore, the CZTSSe phase is actually located at the stoichiometric point. This can be explained that the minimum Gibbs free energy phase must actually sit further towards Cu-poor, Zn-rich composition because of the high vapor pressures of the Sn-S(Se) phases. It is assumed that only the required amount of Sn reacts with available Cu, Zn and S (Se) to form CZTSSe.

3. 2. 4 Electrical properties

The electrical characterization of CZTS_xSe_{1-x} (x=0, 0.2, 0.5, 0.8 and 1.0) single crystal was analysed from Hall effect measurement. The p-type conduction in all samples were observed by using thermoprobe analysis. Figure 10 shows results of Hall effect measurement of CZTSSe single crystal. The each compositional ratios such as Cu/(Zn+Sn), Cu/Zn and Zn/Sn were almost uniform in all samples because the electrical properties have direct correlation with

intrinsic point defects. Especially, we reported the hole concentration p increases with increasing the ratio of Cu/Zn [16]. The hole concentration p values in all samples indicated nearly constant value $(2.2\sim 2.93) \times 10^{17} \text{ cm}^{-3}$. The hole mobility increased with the increasing in the selenium content, which is $10.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for CZTS and $35.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for CZTSe. It was found that CZTS single crystal have high activation energy and a defects path such as hopping conduction in our previous study [16, 17]. Therefore, it is assumed that the difference mobility between CZTS and CZTSe results from the density of bulk defects and the activation energy. The electrical defects level of CZTSSe thin-film solar cell with systematically changed the ratio of S and Se was investigated [30]. In deed, the higher sulfur content in CZTSSe indicated increasing of the trap density as well as high defect energy level. From first-principle calculation, the Cu on Zn antisite defect (Cu_{Zn}) and the Cu vacancy (V_{Cu}) are the dominant acceptor defects in CZTSSe, which leads to p-type conductivity [2]. The Cu_{Zn} level is slightly shallower by 0.04 eV in CZTSe than in CZTS [31]. Thus, the enhancement of conductivity with higher selenium content may be due to lower activation energy and bulk defects density. On the other hand, the band gap energy in CZTS (1.5~1.6 eV) is higher than in CZTSe (0.9~1.0 eV), which have strongly correlation with the potential of solar cell performance such as increasing open-circuit voltage. It is important to systematically investigate the correlation between electrical properties and ratio of S/Se on CZTSSe single crystal in order to achieve higher efficiency CZTSSe solar cell.

4. Conclusions

We investigated the pseudobinary phase diagram of $\text{CZTS}_x\text{Se}_{1-x}$ -Sn system in order to obtain good-quality $\text{CZTS}_x\text{Se}_{1-x}$ single crystal. It is impossible to grow single crystal less than $X=60$ mol% solution because secondary phases (Sn and SnS_x) locate at bottom of ampoules, and interfere with single crystal growth. From the phase diagram, it was possible to grow

CZTSSe single crystals at $X > 60$ mol% and $720 \sim 980^\circ\text{C}$. $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ single crystals ($x=0, 0.2, 0.5, 0.8, 1$) were successfully grown by using traveling heater method on the basis of phase diagram. The optimum condition was the growth temperature 900°C and growth speed $4\sim 5$ mm/day. No secondary phases are observed from XRD and Raman measurements. The FWHM of the XRC for the (112) oriented CZTSSe ($x=0.5$) single crystal is 163 arcsec. The composition of the CZTSe single crystal was homogeneous and the stoichiometric ratio of CZTSe was found to be slightly Cu-poor, Zn-rich, Sn-poor and S (Se)-rich. These results show that good-quality single-phase CZTSSe single crystals can be obtained. The hole carrier concentration p and hole mobility were measured to be $= (2.2\sim 2.93) \times 10^{17} \text{ cm}^{-3}$ and $10.4 \sim 35.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Especially, the hole mobility increased with the increasing in the selenium content. The investigation of high-quality CZTSSe single crystal obtained in this study leads useful understanding to achieve higher performance solar cell.

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Table 1 The liquidus temperature of $\text{CZTS}_{0.5}\text{Se}_{0.5}$ determined by DTA and visually method.

Table 2 The composition results of each phases in Fig. 2.

Table 3 Compositional results of the each compositions of $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.2, 0.5, 0.8, 1.0$) single crystal. Those of CZTS [12] and CZTSe [19] are reported in our previous studies.

<i>X</i> [mol%]	Heating [°C]	Cooling [°C]	Visually [°C]
10	734.1	730.5	725
50	725.4	722.2	720
60	751.4	758.3	760
80	891.6	885.8	895

Table 1 Nagaoka et al.

Number in Fig. 2	Phase	Cu [at.%]	Zn [at.%]	Sn [at.%]	S [at.%]	Se [at.%]
1	Sn solution	5.64	2.53	89.53	1.19	1.11
2	CZTSSe+Sn solution	18.53	11.34	26.42	20.55	23.15
3	CZTSSe+Sn(S,Se) _x +Sn solution	21.73	13.15	22.13	22.85	20.13
4	CZTSSe+Sn solution	21.54	12.55	22.23	24.15	19.53

Table 2 Nagaoka et al.

Composition	Cu	Zn	Sn	S	Se	Cu/(Zn+Sn)	Cu/Zn	Zn/Sn	Ref.
S [x]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]				
0	24.50	13.39	11.26	0	50.85	0.99	1.83	1.19	[19]
0.2	23.65	13.61	11.64	9.67	41.43	0.94	1.74	1.17	
0.5	23.96	13.77	11.42	24.63	26.22	0.95	1.74	1.21	
0.8	23.88	13.13	11.16	41.19	10.64	0.98	1.82	1.18	
1	23.38	12.84	11.13	52.65	0	0.98	1.82	1.15	[12]

Table 3 Nagaoka et al.

Fig. 1 DTA curves of $\text{CZTS}_{0.5}\text{Se}_{0.5}$ in the (a) heating and (b) cooling processes.

Fig. 2 The photographs of synthesized $\text{CZTS}_{0.5}\text{Se}_{0.5}$ ingots cross section ($X=10, 50$ and 90 mol%).

Fig. 3 The powder XRD patterns of $X=50$ and 90 mol% for $\text{CZTS}_{0.5}\text{Se}_{0.5}$ solute.

Fig. 4 The pseudobinary phase diagram of $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.5, 1.0$) -Sn system. That of CZTS [12] and CZTSe [19] are reported in our previous studies.

Fig. 5 A photograph of $\text{CZTS}_{0.5}\text{Se}_{0.5}$ single crystal cross section. The parts of single crystal and solution zone are observed clearly.

Fig. 6 The XRC for (112) oriented $\text{CZTS}_{0.5}\text{Se}_{0.5}$ single crystal.

Fig. 7 The powder XRD pattern of the each compositions $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0.2, 0.5, 0.8$) single crystal.

Fig. 8 Raman spectra of the each compositions of $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.2, 0.5, 0.8, 1.0$) single crystal.

Fig. 9 (a) CZTSSe quaternary phase diagram including two possible pseudo-ternary systems as green ($\text{Cu}(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})$ system) and blue ($\text{Cu}_2(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})_2$ system). The planes intersect along the $\text{Cu}_2\text{Sn}(\text{S}, \text{Se})_3 - \text{CZTSSe} - \text{Zn}(\text{S}, \text{Se})$ tie line. (b) The $\text{Cu}_2(\text{S}, \text{Se}) - \text{Zn}(\text{S}, \text{Se}) - \text{Sn}(\text{S}, \text{Se})_2$ quasi-ternary composition space and plotted grown crystals on.

Fig. 10 The results of Hall effect measurement of $\text{CZTS}_x\text{Se}_{1-x}$ ($x=0, 0.2, 0.5, 0.8, 1.0$) single crystal.

Fig. 1 Nagaoka et al.

$X = 10 \text{ mol\%}$

$X = 50 \text{ mol\%}$

$X = 90 \text{ mol\%}$

Fig. 2 Nagaoka et al.

Fig. 3 Nagaoka et al.

Fig. 4 Nagaoka et al.

Fig. 5 Nagaoka et al.

Fig. 6 Nagaoka et al.

Fig. 7 Nagaoka et al.

Fig. 8 Nagaoka et al.

a)

b)

Fig. 9 Nagaoka et al.

Fig. 10 Nagaoka et al.