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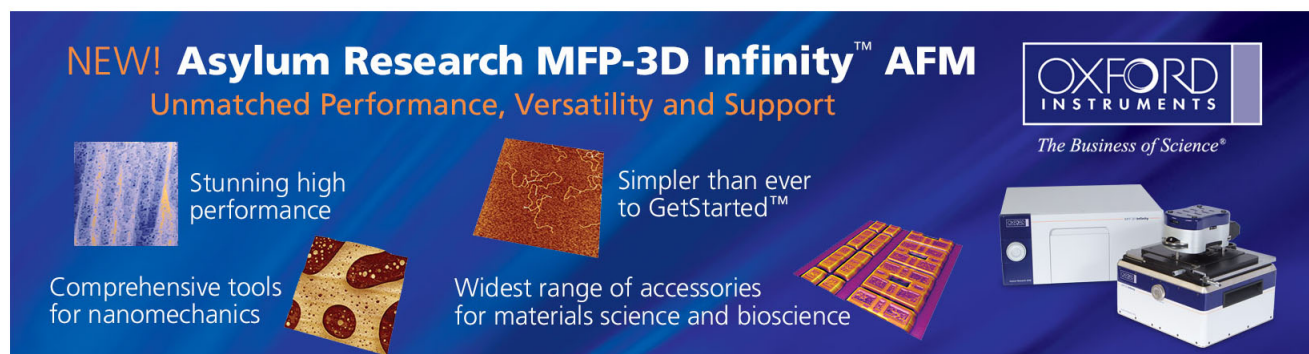
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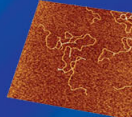
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Effects of sodium on electrical properties in $\text{Cu}_2\text{ZnSnS}_4$ single crystal

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We have studied the effect of sodium on the electrical properties of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) single crystal by using temperature dependence of Hall effect measurement. The sodium substitution on the cation site in CZTS is observed from the increasing of unit-cell size by powder X-ray diffraction. Sodium increases the effective hole concentration and makes the thermal activation energy smaller. The degree of compensation decreases with sodium incorporation, thus the hole mobility is enhanced. We revealed that sodium is important dopant in CZTS to control the electrical properties. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871208>]

The concern of environmental and renewable resource energy has increased, which has the potential to bring modern civilization greater long term economic and geopolitical sustainability than current fossil fuels. The solar cell is the potential candidates and has much drawn attention, recently. The important issue of solar cell would be high efficiency solar cell, a low cost, and non-toxic elements. Recently, the compound semiconductors $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS) and $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe) have extensive been attracted and studied, because their band-gap energies are suitable for solar energy conversion and they have high optical absorption coefficients in the visible spectral regions.¹⁻³ In particular, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is lower cost than CIGS and composed of only earth-abundant elements. Therefore, CZTS is a promising material and achieved important issues for high efficiency solar cell. To date, the best solar cell device conversion efficiency of CZTS-based is about 8.4%,² which is still much lower than the high conversion efficiency of 20.3% obtained for CIGS thin-film solar cells.⁴ To improve the higher efficiency of CZTS-based solar cells, it is necessary to obtain more detailed understanding of the fundamental properties on CZTS.

One reason why that CIGS thin-film solar cell achieved high conversion efficiency includes sodium (Na) effect. Na incorporated into CIGS absorbing layer is well known to have widely valuable effects that lead to enhanced CIGS thin-film solar cell efficiency. The some positive influences of Na on CIGS polycrystalline thin-film have been claimed from previous reports. Na passivates or removes the grain boundary defects such as In antisite on Cu (In_{Cu})⁵ and Se vacancy (V_{Se}).⁶ The oxygen model was suggested that the hole density increases due to the neutralization of donor V_{Se} defects through an enhanced chemisorption of oxygen atom in the presence of Na.⁶ Na replacing a Cu site results in the

formation of a stable compound NaInSe_2 , which indicates a larger band-gap and leads to a larger open-circuit voltage (V_{oc}).⁵ In addition, Na affects the orientation of (112) texture, grain size, and the morphology.^{7,8} It is important to understand Na effects on CZTS in order to improve higher efficiency. Indeed, some effects of Na incorporated into CZTS group material were reported. Na diffusion in CZTS thin-films was found to be enhanced the grain size, the (112) texture of CZTS films, and hole concentration.⁹ Na effects in $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) solar cell were reported that the device efficiency was improved by enhancing the V_{oc} and fill factor.¹⁰ From some reports, it is anticipated that Na may play an important role in CZTS similar to CIGS. We have already obtained high-quality CZTS single crystals from traveling heater method (THM) in order to understand fundamental physical properties.^{11,12} In our previous electrical and optical studies using high-quality CZTS single crystal samples, CZTS have the defect transport (hopping conduction) at low temperature, high activation energy of 130 meV,¹³ and the large-density band tail states formed below the band edge.¹⁴ In addition, to control intrinsic point defects is important because all CZTSSe solar cells with reported efficiencies higher than 8% have Cu-poor, Zn-rich conditions, which indicated a high population of intrinsic defects.¹⁻³ Therefore, it is necessary to investigate the correlation between Na and intrinsic point defects in CZTS, which is significant factor in achieving higher efficiency.

In this Letter, we discuss the effect of Na on electrical properties of CZTS single crystal with a systematic Na concentration control from Hall effect measurement. The investigation of Na effect on electrical properties, such as carrier concentration and mobility, is critically and directly correlated to the higher performance of solar cell devices. The analysis of the temperature dependence of the Hall effect measurement provides valuable information about the electrical conduction mechanism in the CZTS as well as parameters such as the activation energy and acceptor and donor concentrations.

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The Na-doped CZTS single crystals were grown by THM using Na₂S-doped feed CZTS polycrystallines. The prescribed amounts of Cu (5N), Zn (6N), Sn (6N), S (5N) elements and Na₂S powder (2N) were charged into a carbon-coated quartz ampoule under 5.0×10^{-5} Torr. The Na₂S-doped feed CZTS polycrystallines were grown by a melting growth at 1100 °C for 24 h. THM growth condition for single crystals was a Sn solution saturated with 80 mol. % CZTS solute, growth temperature of 900 °C, and a speed of 4–5 mm/day for 10 days. The details of THM and melting growth are shown in our previous studies.^{11,12,15} The detail composition of the single crystal and Na concentration were investigated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The structural characterization of the samples was carried out by powder X-ray diffraction (XRD). The XRD experiments were performed using Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$) and a stepwidth of 0.01°. The XRD patterns were calibrated with a silicon powder (NIST SRM 640d). The heated probe measurement indicated p-type conduction. Hall effect measurements were carried out between 20 and 300 K under 0.54 T magnetic field in the Van der Pauw geometry. The single crystal wafers 10 mm in diameter were cut out from the ingots. The wafers were formed a dimension of 5 mm × 5 mm × 0.5 mm and mechanically polished with 0.01 μm Al₂O₃ powder. Multiple Au contacts of diameter 1 mm were deposited by evaporation onto the corners of each CZTS bulk single crystal to a thickness of 200 nm. The Au contacts indicated Ohmic behavior at all temperatures. The values of resistivity between each Au contacts were homogeneous by applying current and magnetic field reversal, therefore good symmetry was indicated.

The composition results of various Na-doped samples by the ICP-AES measurements are shown in Table I. All samples indicated metallic ratios of $[\text{Cu}]/([\text{Zn}] + [\text{Sn}]) = 0.94\text{--}0.97$, $[\text{Cu}]/[\text{Zn}] = 1.81\text{--}1.86$, and $[\text{Zn}]/[\text{Sn}] = 1.06\text{--}1.10$, which are slightly Cu-poor, Zn-rich conditions. The presence of Na with 0.04 and 0.13 mol. % in single crystal was observed, which is most important in this study.

The transport mechanisms can be described by a two-path system using hopping and typical thermal activation conduction in our previous report.¹³ Therefore, the carrier concentration p is given by¹⁶

$$p = -A + \sqrt{A^2 + gN_V(N_A - N_D)\exp(-E_a/k_B T)}, \quad (1)$$

$$A = \frac{1}{2}[N_D + gN_V \exp(-E_a/k_B T)],$$

where p is hole concentration in valence band, N_V is the effective density of states in the valence band, N_A is the

TABLE I. The composition results of various Na-doped CZTS single crystal samples by the ICP-AES measurements. The ratio of Cu/(Zn + Sn) = 0.95 – 0.98 in this study is almost constant and slightly Cu-poor, Zn-rich condition.

Na [mol. %]	[Cu]/([Zn] + [Sn])	[Cu]/[Zn]	[Zn]/[Sn]
Non	0.947	1.806	1.101
0.04	0.955	1.857	1.058
0.13	0.977	1.862	1.104

acceptor, N_D is the donor concentration, E_a is the acceptor activation energy, k_B is Boltzmann constant, and g is the degeneracy factor = 1/2. Typically, R_H is defined r_H/ep , where r_H is the Hall scattering factor and e is the elementary charge. In two-mechanism case, we determined that r_H equals 1. N_V have temperature dependence of $\sim T^{3/2}$, however, it may be difficult to determine N_V value because the large-density band tail states formed below the band edge in our reports.¹⁴ In this study, N_V is constants ($1.6 \times 10^{19} \text{ cm}^{-3}$) in non-doped sample.

The temperature dependence of the hole concentration p for various Na compositions of CZTS single crystals, obtained using Eq. (1), and their parameters, are shown in Fig. 1 and Table II, respectively. The hole concentration p is enhanced with increasing Na concentration similar to previous CIGS reports.^{16,17} This is simply assumed that Na may form the cation-antisite defects, because the effect in grain boundary is neglected due to the single crystal nature of the CZTS in this study. In addition, the increasing of dominant acceptor defect in CZTS from first principle calculation such as Cu vacancy (V_{Cu}) and Cu on Zn antisite (Cu_{Zn}) may not be expected because metallic ratios of $[\text{Cu}]/([\text{Zn}] + [\text{Sn}])$, $[\text{Cu}]/[\text{Zn}]$, and $[\text{Zn}]/[\text{Sn}]$ are nearly homogeneous in all samples.¹⁸ Indeed, our previous study reported the p values at room temperature increase with higher ratio of $[\text{Cu}]/[\text{Zn}]$.¹³ Figure 2 shows the (112) peaks shifts calibrated by Si peaks as an internal reference. A significant observation from XRD pattern is that there seems to be an apparent enhancement in unit-cell size with increasing of Na concentration, where non-doped unit-cell is 319.6 \AA^3 and that of the 0.13 mol. % doped is 324.7 \AA^3 . This result revealed that Na is substitutional impurity in CZTS because radius of Na atom is greater than that of cations in CZTS.

The thermal activation energy E_a , as determined by the temperature dependence of the hole concentration, is smaller with increasing Na concentration (N_A concentration). A large number of different effects have been suggested in order to

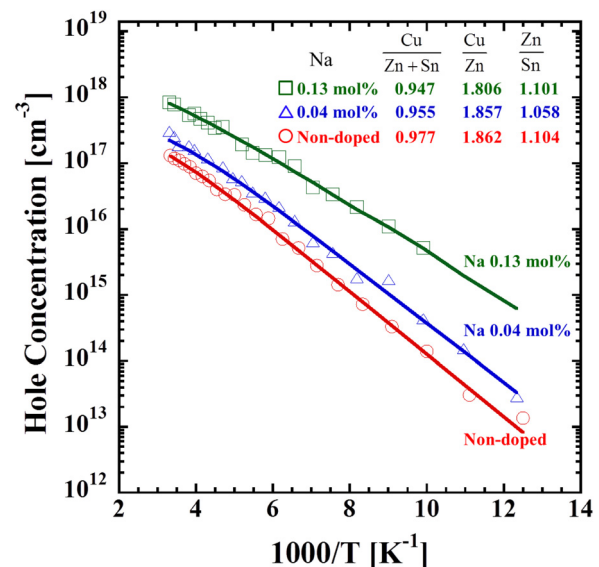


FIG. 1. The temperature dependence of the hole concentration for variations in Na composition of CZTS single crystals using Eq. (1). The ratios of metal composition were nearly homogeneous in order to investigate Nature Na effect. The hole concentration p increased with increasing Na concentration.

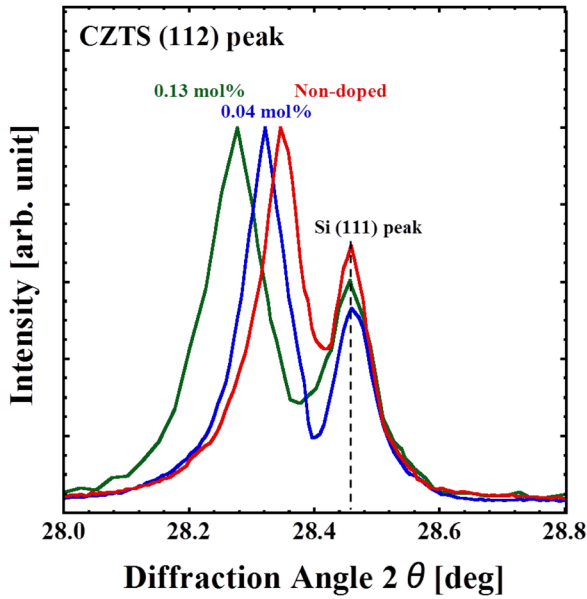


FIG. 2. The (112) peaks shifts calibrated by Si peaks as an internal reference. A systematic shift of peaks toward lower angle values in samples containing Na is evidence of the increasing of unit-cell size.

explain theoretically the concentration dependence of E_a .^{19–21} Empirically, E_a linearly depends on the third root of the acceptor concentration $N_A^{1/3}$ and shown in Fig. 3, which is described by^{19,20}

$$E_a = E_{a0} - \alpha N_A^{1/3}, \quad (2)$$

where E_{a0} is the thermal activation energy in the infinite dilution limit. An infinite dilution limit of the activation energy E_{a0} of 116 ± 2 meV and a linear dependence with a slope α of $(2.09 \pm 0.1) \times 10^{-8}$ eV cm were found from Eq. (2). Especially, E_{a0} value of 116 meV in this work corresponds well to that of 110 meV in our previous non-doped single crystal report.¹³ These results reveal that non- and doped CZTS single crystal samples have the same acceptor defect with an activation energy around 113 ± 3 meV. In addition, E_a value is smaller with increasing Na concentration and makes Fermi level toward the valence band, which leads to higher built-in voltage and achieves higher V_{OC} .

Temperature dependence of the hole mobility μ in Na-doped and non-doped CZTS single crystal is shown in Fig. 4. The hole mobility μ is enhanced from 9.4 to $16.4 \text{ cm}^2/\text{V s}$ with increasing Na concentration. We focus on low temperature region below 100 K, where the defect scattering is dominant. The lines included in Fig. 4 are the fits to $\mu \sim T^x$. At low temperature x values of non-doped sample are 2.3 and larger than typical value 1.5.²² This indicates the

TABLE II. The parameters to fit the temperature dependent hole concentration.

Na [mol. %]	N_V [cm^{-3}]	N_A [cm^{-3}]	N_D [cm^{-3}]	K (N_D/N_A)	E_a [meV]
Non	1.60×10^{19}	1.51×10^{18}	8.10×10^{17}	0.536	94.0
0.04	1.60×10^{19}	1.70×10^{18}	6.94×10^{17}	0.408	89.1
0.13	1.60×10^{19}	9.52×10^{18}	2.88×10^{18}	0.303	71.9

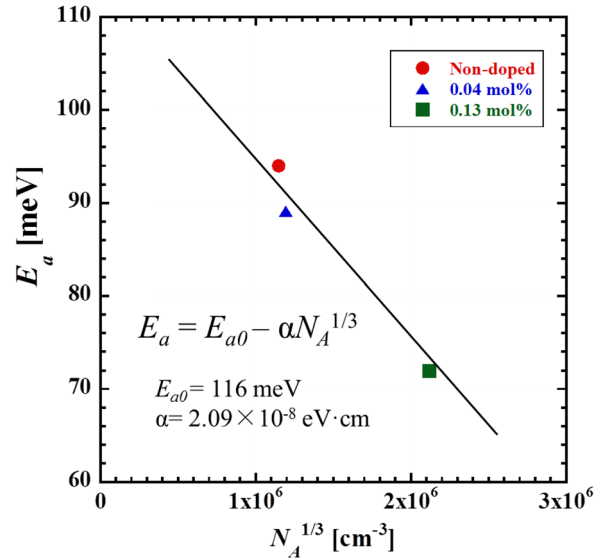


FIG. 3. The thermal activation energy E_a linearly depends on the third root of the acceptor concentration $N_A^{1/3}$. E_a is smaller with increasing Na concentration.

steep decrease of the mobility with decreasing temperature, which is typical hopping conduction.^{16,23,24} The x values decrease with Na concentration from 2.3 to 1.7. Furthermore, the degree of compensation K ($=N_D/N_A$) also decreased with increasing Na concentration from 0.5 to 0.3 in Table II. Those results indicate the defects scattering decrease. The higher temperature lines around room temperature follow a $T^{-0.9}$ behavior in all samples, where the lattice scattering is dominant. Therefore, the defect scattering is more dominant than the lattice scattering in CZTS. The reducing in the degree of compensation K is somewhat surprising given that the expected role of Na is as either a

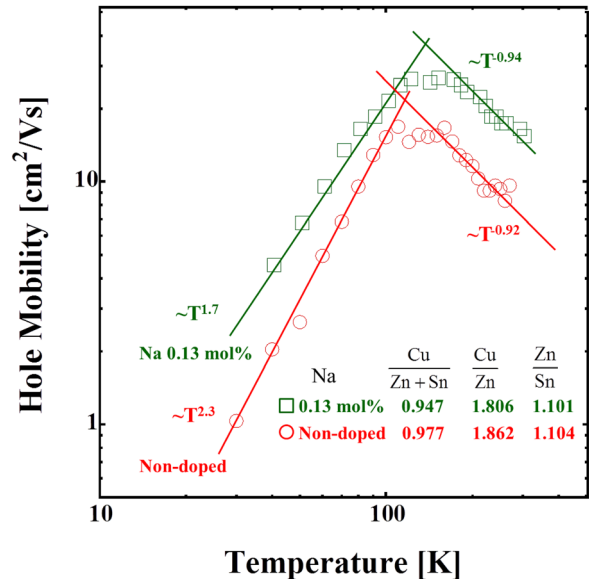


FIG. 4. Temperature dependence of the hole mobility μ in Na-doped and non-doped CZTS single crystal. At low temperature x values of non-doped sample are 2.3 and larger than typical value 1.5. The hole mobility μ is enhanced with increasing Na concentration and indicates hopping conduction at low temperature. This is because the degree of compensation K is smaller and the defects scattering decreases with the Na incorporation into CZTS.

substitution on cations in CZTS. From first principle calculation, Zn on antisite Cu (Zn_{Cu}) is dominant donor defects in CZTS. We believed that the formation of the Zn_{Cu} donor defects is inhibited by a finite Na substitution for the Zn_{Cu} antisites ($=Na_{Cu}$). Therefore, the results are the increasing of effective hole concentration and the decreasing of compensation. In CIGS study, Contreras *et al.* suggested that the increasing of the effective acceptor concentration is because In on antisite Cu (In_{Cu}) dominant donor defect in CIGS is inhibited by a finite Na substitution for the In_{Cu} antisites ($=Na_{Cu}$), which is called *the In_{Cu} model*.²⁵ Indeed, on experimental results of CZTSSe group, Li *et al.* reported that the concentration of certain deep level defects in CZTSe thin-films with increasing Na concentration, and the hole mobility is enhanced.¹⁰ It is difficult to conclude that Na replaces with intrinsic acceptor (V_{Cu} or Cu_{Zn}) or donor (Zn_{Cu}), even though the enhancement of unit-cell size in CZTS with increasing of Na concentration was observed. However, it revealed that Na plays role of enhancement of effective hole concentration and mobility on CZTS. These results indicate the possibility of improvement of CZTS solar cell efficiency.

In conclusion, we have studied the effect of Na incorporation in CZTS single crystal and influence on the electrical properties using the temperature dependence of Hall effect measurements. The ratios of metal composition were nearly homogeneous in order to investigate nature Na effect because CZTS have a lot of intrinsic point defects. We observed the expansion of unit-cell in Na-doped CZTS by powder XRD measurement, which is evidence of Na on antisite cations in CZTS. The hole concentration p increased with increasing Na concentration and makes the thermal activation energy E_a is smaller, which leads to higher built-in voltage. This finding gives the possibility of achieving higher V_{OC} by optimization of Na incorporation. All CZTS samples have the same acceptor defect with an activation energy around $E_{a0} = 120$ meV in the infinite dilution limit, which is good agreement with various composition non-doped CZTS single crystal results. The hole mobility μ is enhanced with increasing Na concentration and indicates hopping conduction at low temperature. This is because the degree of compensation K is smaller and the defects scattering decreases with the Na incorporation into CZTS. However, it is not possible to determine that Na creates new acceptor or removes the donor defects. In this study, we revealed that Na is important dopant in CZTS single crystal to control the electrical properties and provided useful understanding to improve higher efficiency of CZTS solar cell.

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