**Supporting Information**

**Title**

# Supporting Information of "Novel spinel-type selenide semiconductor $ZnSc_2Se_4$ and its solid solution with sulfide for photovoltaics"

**Authors**

Kota Hanzawa[1], Ryoga Nagasawa[1], and Hidenori Hiramatsu[1,2,*]

**Affiliations**

1 Materials and Structures Laboratory, Institute of Integrated Research, Institute of Science Tokyo, 4259 Nagatsuta, Midori, Yokohama 226-8501, Japan

2 MDX Research Center for Element Strategy, Institute of Integrated Research, Institute of Science Tokyo, 4259 Nagatsuta, Midori, Yokohama 226-8501, Japan

Correspondence and requests for materials should be addressed to H. Hiramatsu.

*Hidenori Hiramatsu hiramatsu.h.aa@m.titech.ac.jp

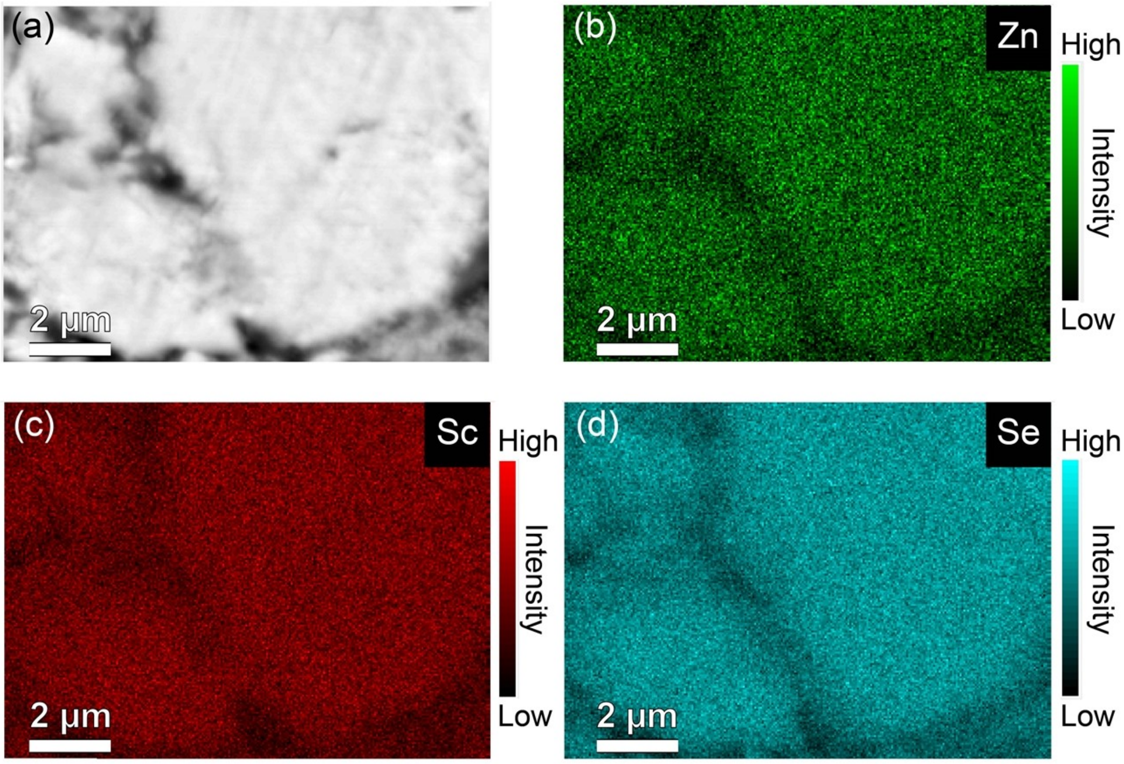

Figure S1. Chemical composition analysis of the $ZnSc_2Se_4$ bulk synthesized at 5.0 GPa and $y = 0.5$ using EPMA. (a) Electron micrograph. White and black regions correspond to main phase ($ZnSc_2Se_4$) and void space, respectively. Element maps of (b) Zn, (c) Sc, and (d) Se. The vertical color bars are indicators of signal intensity from each element.

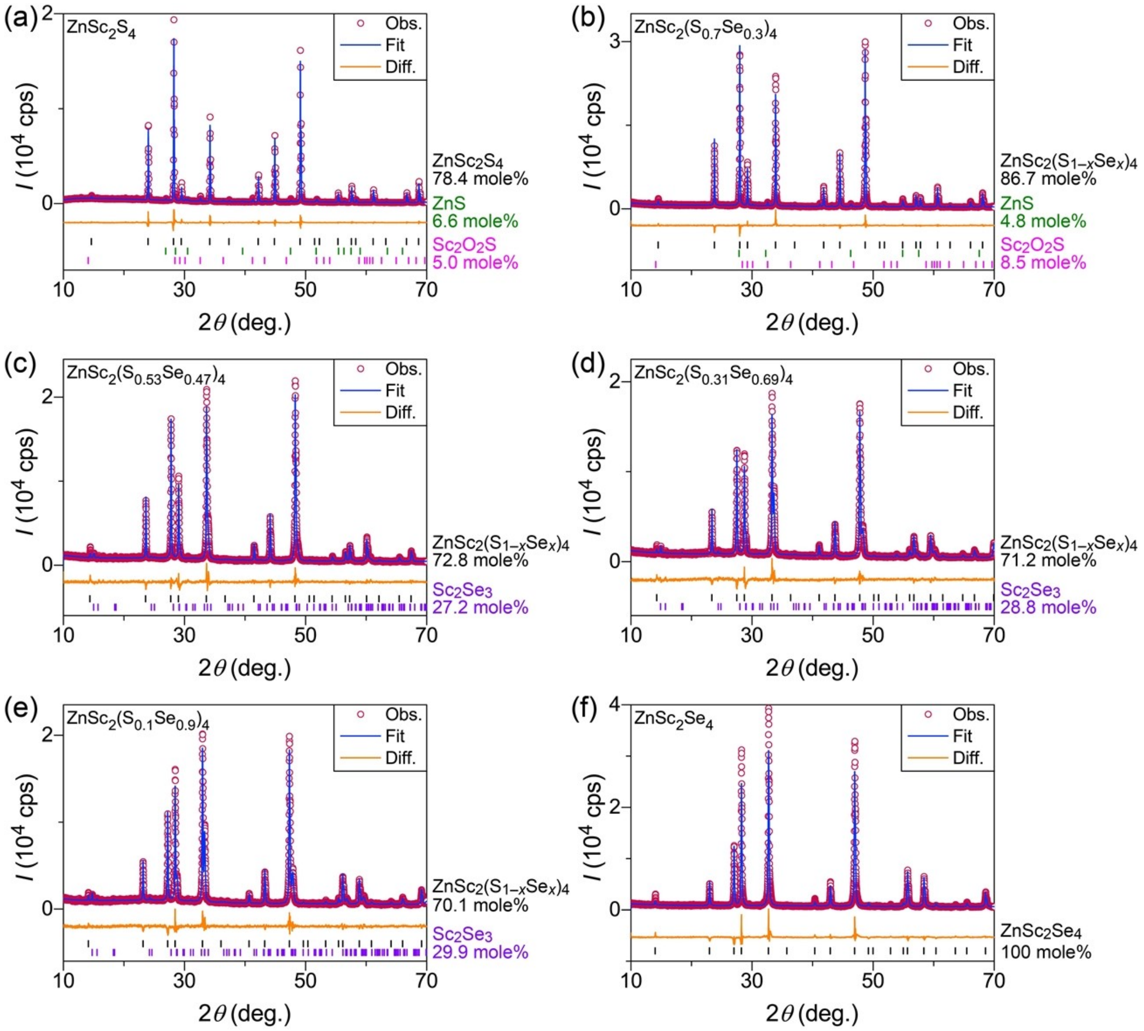

**Figure S2.** Rietveld refinement results of XRD patterns for $ZnSc_2(S_{1-x}Se_x)_4$ ($x = 0$–$1$) samples. Red circles, blue line, and orange line represent experimentally observed XRD pattern, fitted pattern by the Rietveld refinement, and difference between them, respectively. Diffraction angles of detected phases are denoted by vertical bars colored black for $ZnSc_2(S_{1-x}Se_x)_4$, green for ZnS, pink for $Sc_2O_2S$, and purple for $Sc_2Se_3$. The chemical composition shown on the upper left in each figure is based on the result of refinement. The mole fraction of each phase is shown on the bottom right side of the figure.

**Table 1.** Summary of Rietveld Refinements for XRD Patterns of $ZnSc_2(S_{1-x}Se_x)_4$ ($x$ = 0–1): *a*-axis Lattice Parameter (*a*), Multiplicities and Wyckoff Notations (WN), Site Occupancies (*g*), Fractional Coordinates (*x*, *y*, *z*), and Isotropic Displacement Parameters (*B*). Values in Parentheses Are Standard Deviations in the Last One or Two digits.

| Nominal composition | Refined formula | *a* (Å) | Sites | WN | *g* | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| $ZnSc_2S_4$ | $ZnSc_2S_4$ | 10.49116(10) | | | | | | | |
| | | | Zn | 8b | 1 | 0.375 | 0.375 | 0.375 | 0.96(7) |
| | | | Sc | 16c | 1 | 0 | 0 | 0 | 0.35(7) |
| | | | S | 32e | 1 | 0.24479(18) | 0.24479(18) | 0.24479(18) | 0.230(7) |
| $ZnSc_2(S_{0.8}Se_{0.2})_4$ | $ZnSc_2(S_{0.7}Se_{0.3})_4$ | 10.57161(7) | | | | | | | |
| | | | Zn | 8b | 1 | 0.375 | 0.375 | 0.375 | 2.46(5) |
| | | | Sc | 16c | 1 | 0 | 0 | 0 | 0.30(4) |
| | | | S | 32e | 0.702(3) | 0.24580(8) | 0.24580(8) | 0.24580(8) | 1.17(3) |
| | | | Se | 32e | 0.298(3) | 0.24580(8) | 0.24580(8) | 0.24580(8) | 1.17(3) |
| $ZnSc_2(S_{0.6}Se_{0.4})_4$ | $ZnSc_2(S_{0.53}Se_{0.47})_4$ | 10.66192(16) | | | | | | | |
| | | | Zn | 8b | 1 | 0.375 | 0.375 | 0.375 | 2.71(9) |
| | | | Sc | 16c | 1 | 0 | 0 | 0 | 0.30(6) |
| | | | S | 32e | 0.529(5) | 0.24570(11) | 0.24570(11) | 0.24570(11) | 1.08(5) |
| | | | Se | 32e | 0.471(5) | 0.24570(11) | 0.24570(11) | 0.24570(11) | 1.08(5) |
| $ZnSc_2(S_{0.4}Se_{0.6})_4$ | $ZnSc_2(S_{0.31}Se_{0.69})_4$ | 10.75713(13) | | | | | | | |
| | | | Zn | 8b | 1 | 0.375 | 0.375 | 0.375 | 3.77(9) |
| | | | Sc | 16c | 1 | 0 | 0 | 0 | 0.30(6) |
| | | | S | 32e | 0.312(6) | 0.24624(10) | 0.24624(10) | 0.24624(10) | 1.12(3) |
| | | | Se | 32e | 0.688(6) | 0.24624(10) | 0.24624(10) | 0.24624(10) | 1.12(3) |
| $ZnSc_2(S_{0.2}Se_{0.8})_4$ | $ZnSc_2(S_{0.1}Se_{0.9})_4$ | 10.85991(13) | | | | | | | |
| | | | Zn | 8b | 1 | 0.375 | 0.375 | 0.375 | 3.37(10) |
| | | | Sc | 16c | 1 | 0 | 0 | 0 | 0.30(6) |
| | | | S | 32e | 0.100(6) | 0.24546(8) | 0.24546(8) | 0.24546(8) | 0.81(3) |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Se | 32e | 0.900(6) | 0.24546(8) | 0.24546(8) | 0.24546(8) | 0.81(3) |
| $ZnSc_2Se_4$ | $ZnSc_2Se_4$ | 10.94163(17) |  |  |  |  |  |  |  |
|  |  |  | Zn | 8b | 1 | 0.375 | 0.375 | 0.375 | 5.00(13) |
|  |  |  | Sc | 16c | 1 | 0 | 0 | 0 | 0.38(7) |
|  |  |  | Se | 32e | 1 | 0.24624(10) | 0.24624(10) | 0.24624(10) | 0.68(3) |

**Table S2.** Reliability Factor (*R*) of Rietveld Refinements for XRD Patterns of $ZnSc_2(S_{1-x}Se_x)_4$ ($x = 0–1$), Including *R*-weighted pattern ($R_{wp}$), *R*-pattern ($R_p$), *R*-expected ($R_e$), and Goodness of Fit ($S = R_{wp} / R_e$)

| Refined formula | $ZnSc_2S_4$ | $ZnSc_2(S_{0.7}Se_{0.3})_4$ | $ZnSc_2(S_{0.53}Se_{0.47})_4$ | $ZnSc_2(S_{0.31}Se_{0.69})_4$ | $ZnSc_2(S_{0.1}Se_{0.9})_4$ | $ZnSc_2Se_4$ |
|---|---|---|---|---|---|---|
| Nominal composition | $ZnSc_2S_4$ | $ZnSc_2(S_{0.8}Se_{0.2})_4$ | $ZnSc_2(S_{0.6}Se_{0.4})_4$ | $ZnSc_2(S_{0.4}Se_{0.6})_4$ | $ZnSc_2(S_{0.2}Se_{0.8})_4$ | $ZnSc_2Se_4$ |
| $R_{wp}$ (%) | 11.80 | 9.37 | 10.03 | 8.48 | 7.90 | 13.36 |
| $R_p$ (%) | 8.31 | 7.06 | 6.74 | 6.43 | 6.22 | 9.77 |
| $R_e$ (%) | 4.97 | 9.52 | 8.55 | 8.08 | 7.81 | 7.41 |
| $S$ | 2.37 | 0.98 | 1.17 | 1.05 | 1.01 | 1.80 |

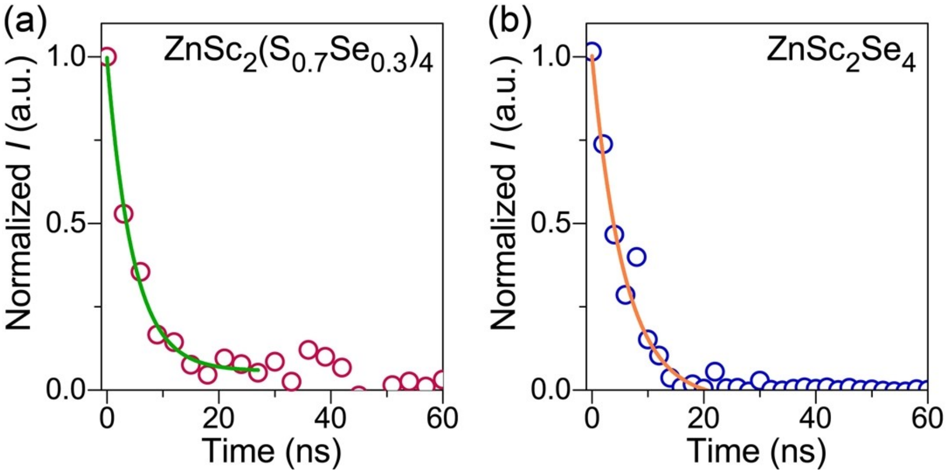

**Figure S3.** Decay curves of the PL on (a) $ZnSc_2(S_{0.7}Se_{0.3})_4$ and (b) $ZnSc_2Se_4$. Solid curves show fitting results using a single decay model: $I = I_0\exp(-t/\tau)$, where $I_0$ is the initial intensity at time ($t$) = 0 and $\tau$ is the PL lifetime.