

Supporting Information

A Pseudo-Binary Approach to the Discovery and Design of Copper-based Sulphides

Takashi Hagiwara,¹ Koichiro Suekuni,^{1,2*} Pierric Lemoine,^{3,4**†} Carmelo Prestipino,³ Erik Elkaim,⁵ Andrew R. Supka,⁶ Rabih Al Rahal Al Orabi,⁶ Marco Fornari,^{6*} Emmanuel Guilmeau,^{7*} Bernard Raveau,⁷ Hikaru Saito,⁸ Philipp Sauerschnig,⁹ Michihiro Ohta,⁹ Yui Kanemori,¹⁰ and Michitaka Ohtaki^{1,2}

1 Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816–8580, Japan

2 Transdisciplinary Research and Education Center for Green Technologies, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

3 Université de Rennes 1, CNRS, ISCR-UMR 6226, F-35000 Rennes, France

4 Institut Jean Lamour, UMR7198 CNRS, Université de Lorraine, 54011 Nancy, France

5 Synchrotron Soleil, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France

6 Department of Physics and Science of Advanced Materials Program, Central Michigan University, Mt. Pleasant, Michigan 48859, USA

7 CRISMAT, CNRS, Normandie Université, ENSICAEN, UNICAEN, 14000 Caen, France

8 Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

9 Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8569, Japan

10 Department of Energy Science and Engineering, Faculty of Engineering, Kyushu University, Motoooka, Fukuoka, 819-0395, Japan

*Koichiro Suekuni – suekuni.koichiro.063@m.kyushu-u.ac.jp

**Pierric Lemoine – pierric.lemoine@univ-lorraine.fr

*Emmanuel Guilmeau – emmanuel.guilmeau@ensicaen.fr

*Marco Fornari – fornari1m@cmich.edu

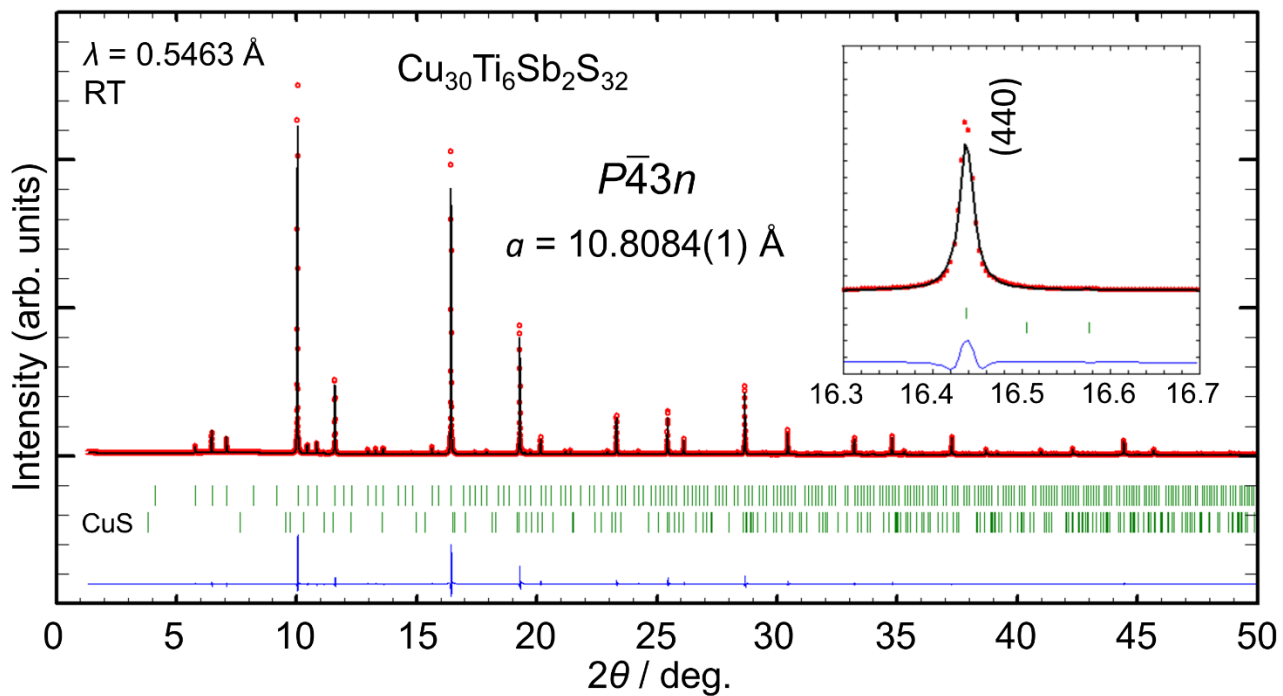


Figure S1. Rietveld analysis of synchrotron PXRD pattern for the hot press sample of $\text{Cu}_{30}\text{Ti}_6\text{Sb}_2\text{S}_{32}$.

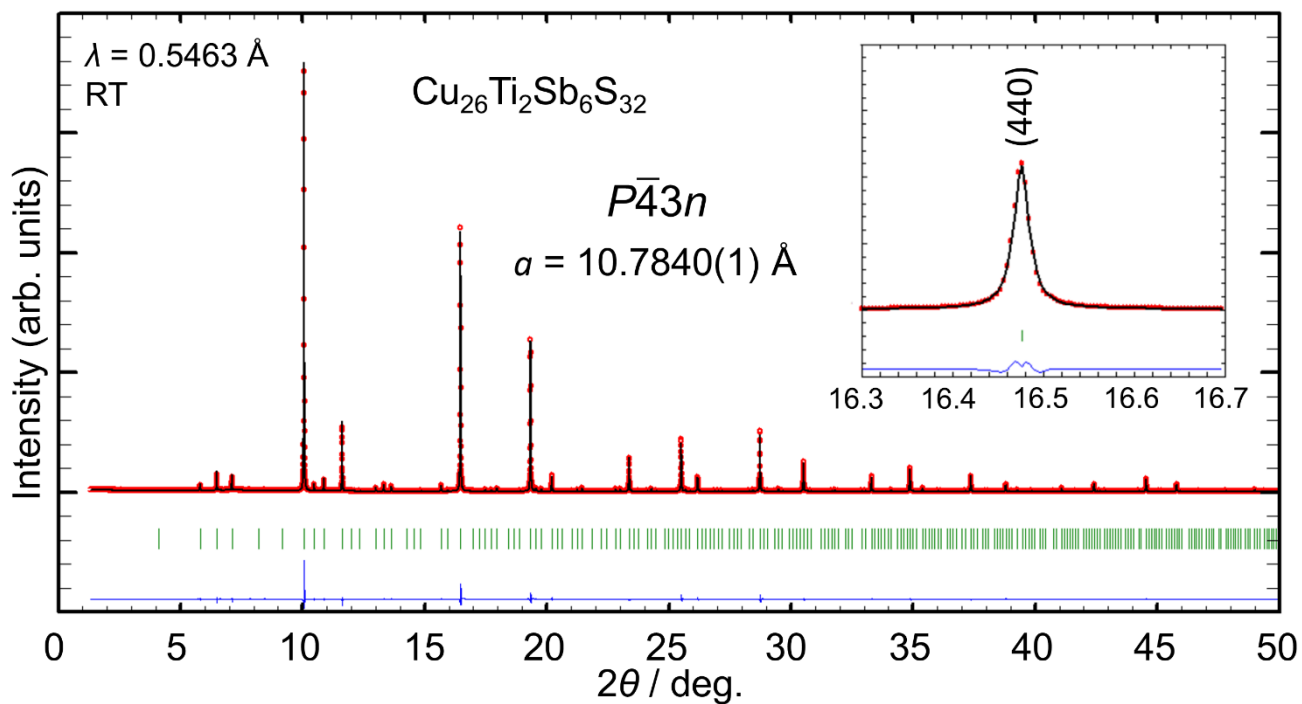


Figure S2. Rietveld analysis of synchrotron PXRD pattern for the hot press sample of $\text{Cu}_{26}\text{Ti}_2\text{Sb}_6\text{S}_{32}$.

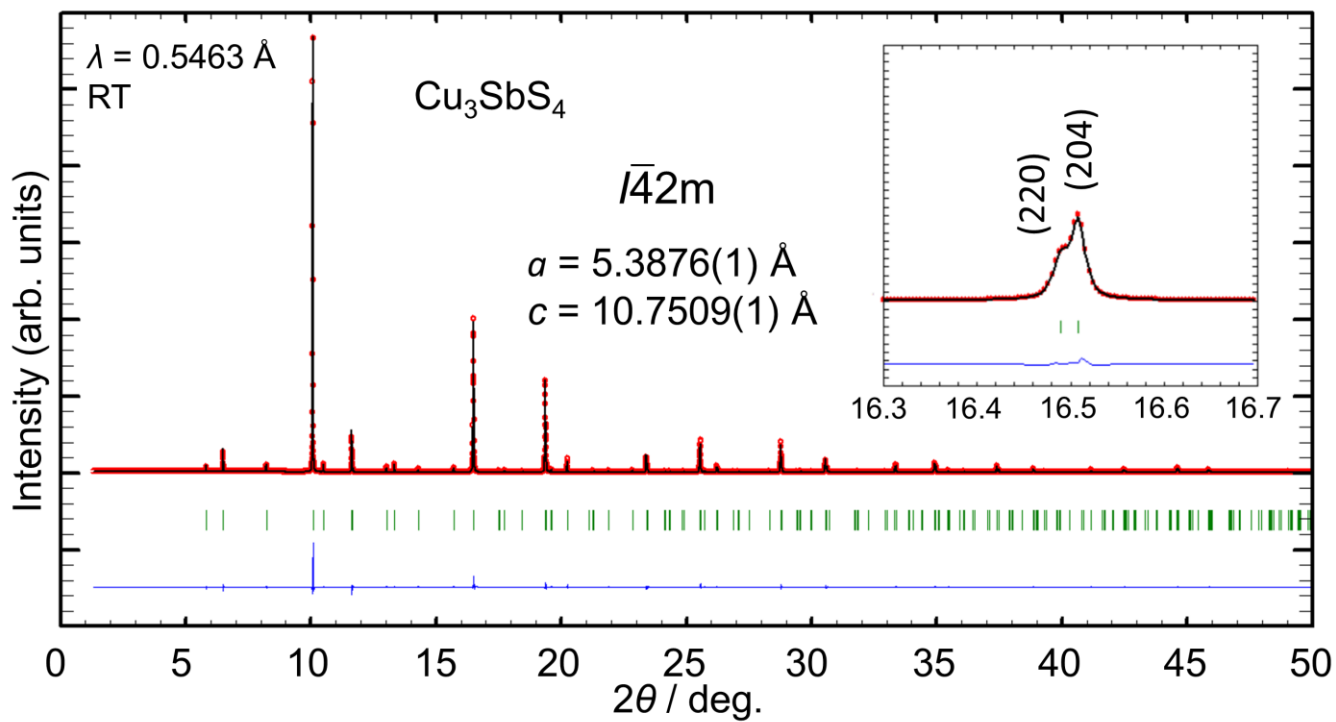


Figure S3. Rietveld analysis of synchrotron PXRD pattern for the hot press sample of Cu_3SbS_4 .

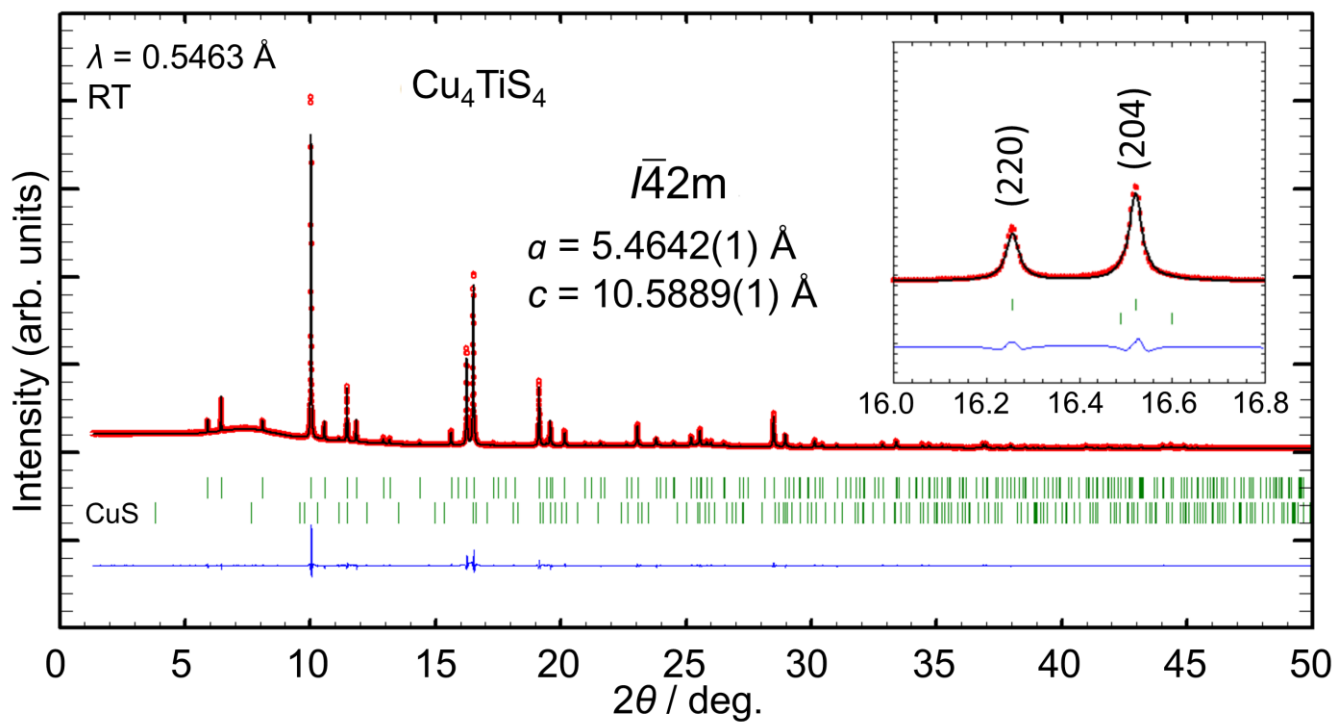


Figure S4. Rietveld analysis of synchrotron PXRD pattern for the hot press sample of Cu_4TiS_4 .

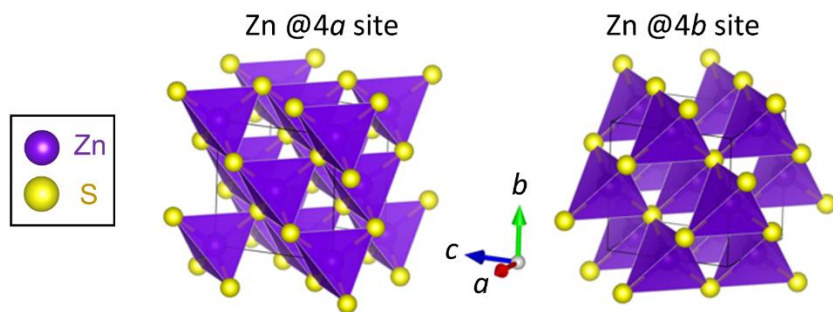


Figure S5. Crystal structure representations of sphalerite (ZnS).

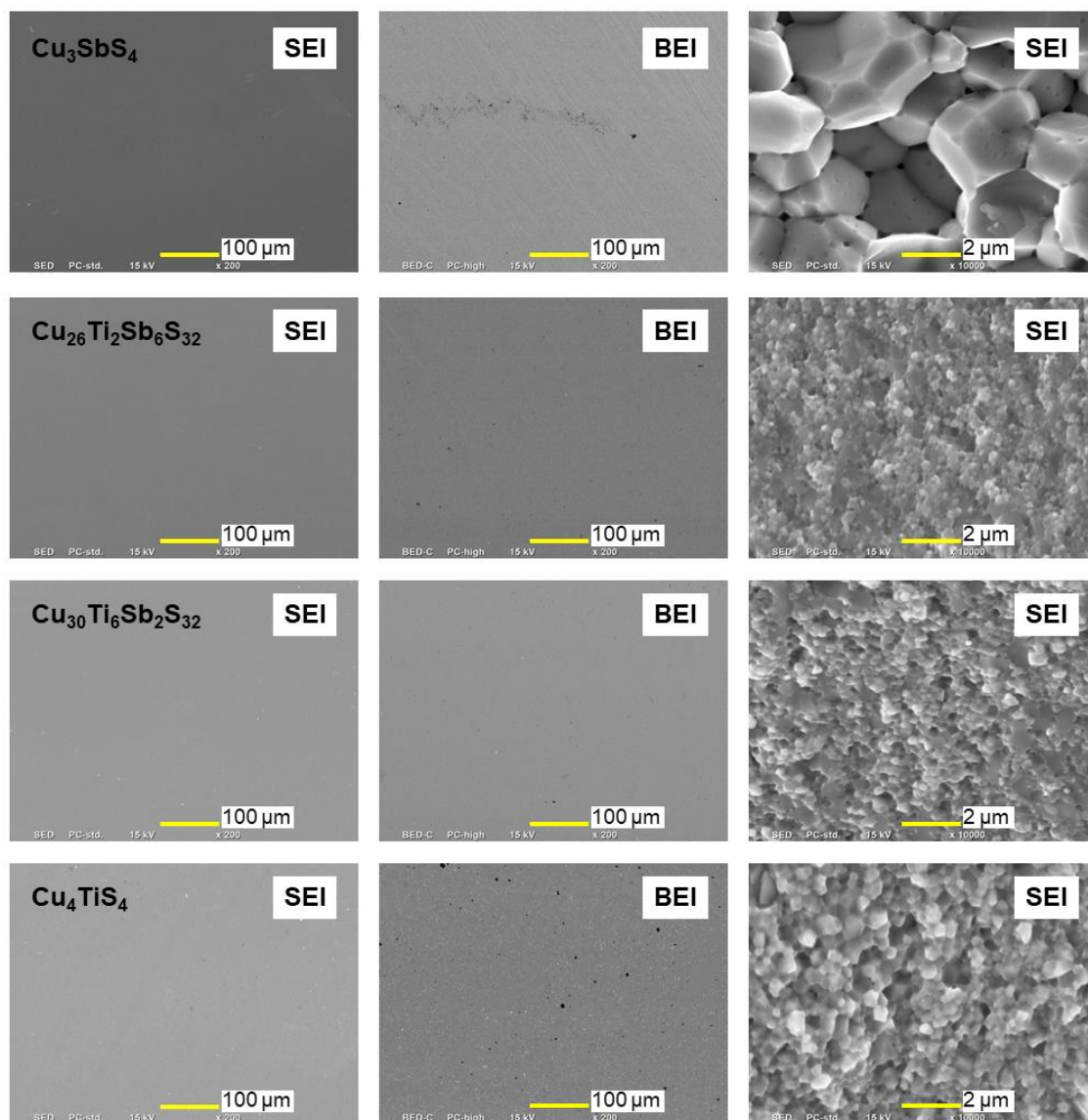


Figure S6. Secondary electron images (SEI, left) and Backscattered electron images (BEI, center) for polished surface, and SEIs for fractured surface (right) of hot-press samples of Cu_3SbS_4 , $\text{Cu}_{26}\text{Ti}_2\text{Sb}_6\text{S}_{32}$, $\text{Cu}_{30}\text{Ti}_6\text{Sb}_2\text{S}_{32}$ and Cu_4TiS_4 .

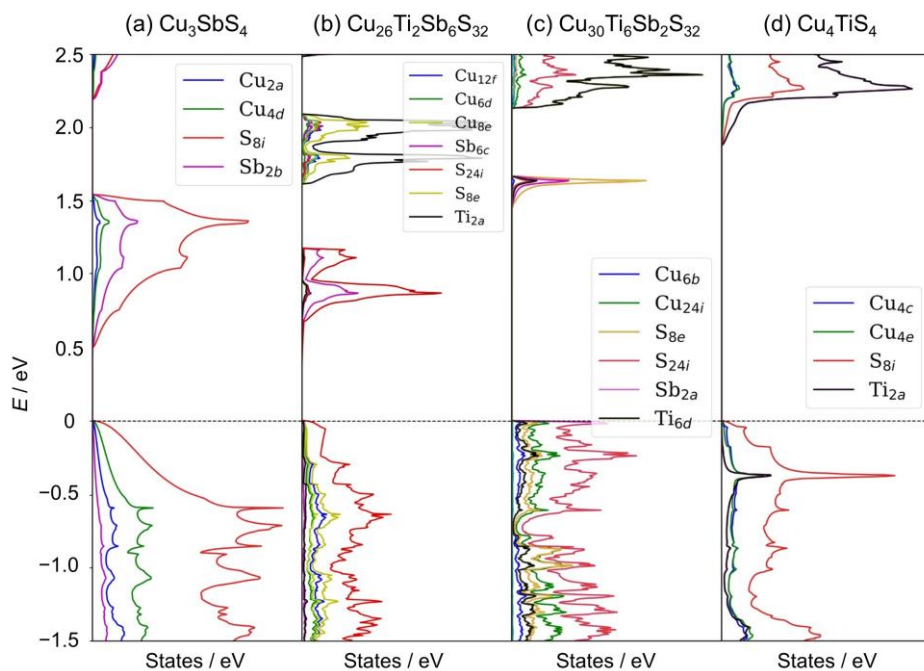


Figure S7. Atom-projected electron density of states calculated for Cu_3SbS_4 , $\text{Cu}_{26}\text{Ti}_2\text{Sb}_6\text{S}_{32}$, $\text{Cu}_{30}\text{Ti}_6\text{Sb}_2\text{S}_{32}$, and Cu_4TiS_4 .

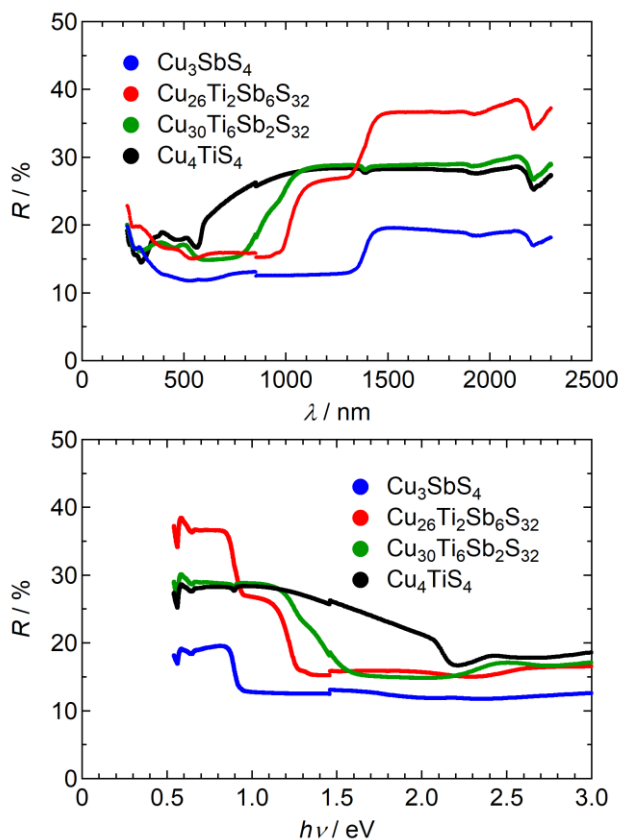


Figure S8. Diffuse reflectance spectra for the annealed (w/o sintering) samples of Cu_3SbS_4 , $\text{Cu}_{26}\text{Ti}_2\text{Sb}_6\text{S}_{32}$, $\text{Cu}_{30}\text{Ti}_6\text{Sb}_2\text{S}_{32}$ and Cu_4TiS_4 . The reflectance is plotted with respect to the wavelength (top) and energy (bottom) of the incident light.

Table S1. Hubbard U (eV) correction computed with the ACBN0 approach for Cu_3SbS_4 , $\text{Cu}_{26}\text{Ti}_2\text{Sb}_6\text{S}_{32}$, $\text{Cu}_{30}\text{Ti}_6\text{Sb}_2\text{S}_{32}$ and Cu_4TiS_4 .

Cu_3SbS_4 ($I\bar{4}2m$)

| Cu (2a) | Cu (4d) | Sb (2b) | S (8i) |
|---------|---------|---------|--------|
| 7.76 | 7.65 | 0.01 | 1.64 |

$\text{Cu}_{26}\text{Ti}_2\text{Sb}_6\text{S}_{32}$ ($P\bar{4}3n$)

| Cu (12f) | Cu (6d) | Cu (8e) | Ti | Sb | S (24i) | S (8e) |
|----------|---------|---------|-------|-------|---------|--------|
| 7.995 | 7.565 | 7.780 | 0.009 | 0.005 | 1.483 | 1.643 |

$\text{Cu}_{30}\text{Ti}_6\text{Sb}_2\text{S}_{32}$ ($P\bar{4}3n$)

| Cu (6b) | Cu (24i) | Ti (6d) | Sb (2a) | S (8e) | S (24i) |
|---------|----------|---------|---------|--------|---------|
| 8.56 | 8.55 | 0.04 | 0.00 | 1.38 | 1.57 |

Cu_4SbS_4 ($I\bar{4}2m$)

| Cu (4c) | Cu (4e) | Ti (2a) | S (8i) |
|---------|---------|---------|--------|
| 8.97 | 8.99 | 0.10 | 1.67 |