龍谷大学
RYUKOKU UNIVERSITY

Analysis for chemical bonds in $Cu(In,Ga)(S,Se)_2$ using Low-temperature XAFS

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Compound photovoltaic device material $CuInSe_2$

CIS has an absorption efficiency of one-hundredth times of that of silicon.

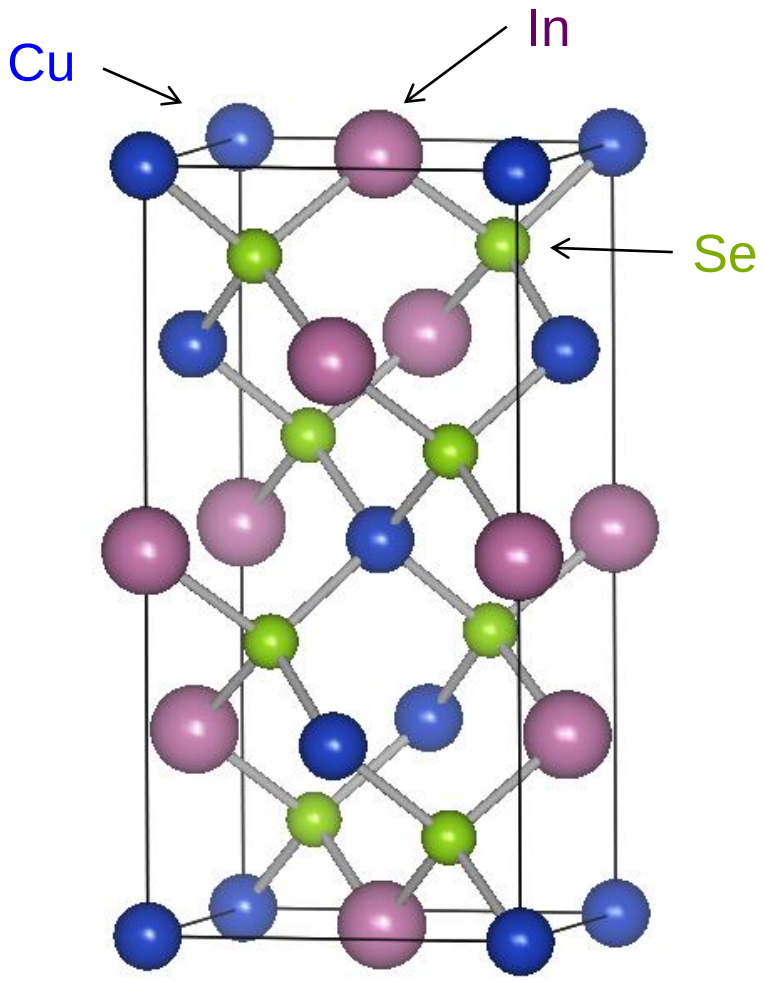
CIS and related compound have attracted much attention as alternative materials for silicon solar cell.

$Cu(In,Ga)(S,Se)_2$ thin-film photovoltaic device achieves 23.35% conversion efficiency.

Solar Frontier, Press released, 2019.1.17,
http://www.solar-frontier.com/jpn/news/2019/0117_press.html
N. Motoshi et al., IEEE J. Photovoltaics 9 (6), 1863 (2019).

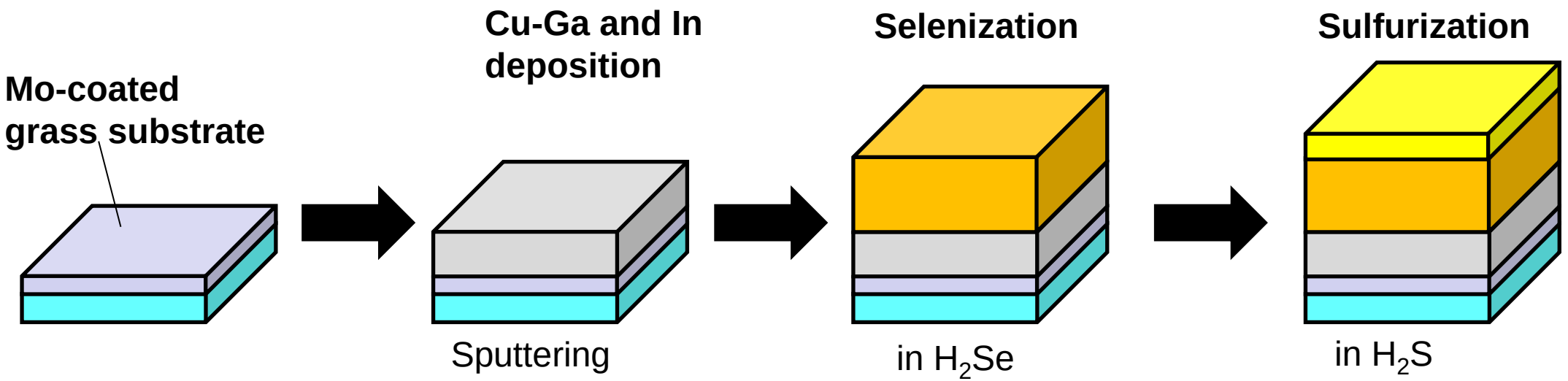
- $CuInSe_2$ (CIS) has chalcopyrite-type structure.
- The chalcopyrite-type structure has two kinds of chemical bonds, Cu-Se and In-Se.

Crystal structure of $CuInSe_2$



Fabrication method of $Cu(In,Ga)(S,Se)_2$ films

- **Selenization and sulfurization process**



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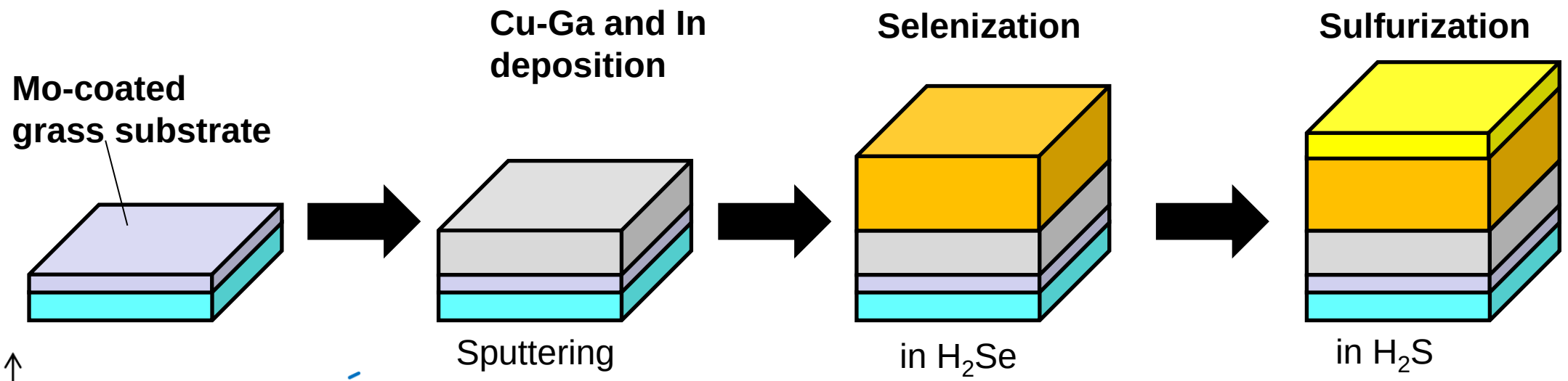
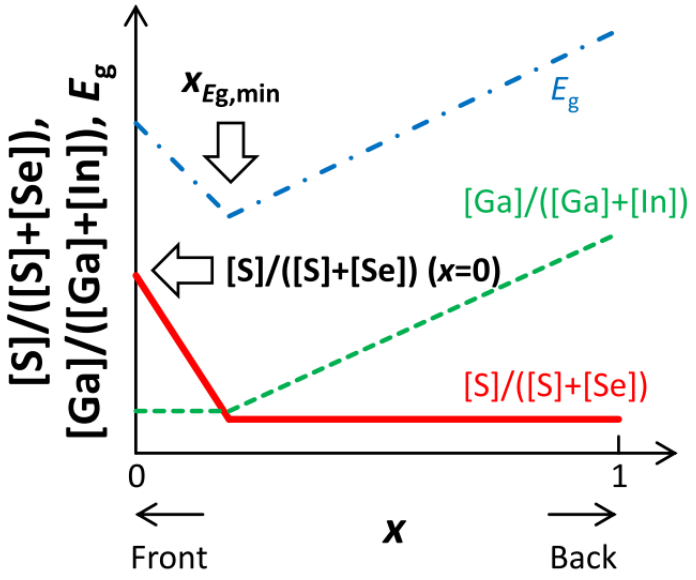
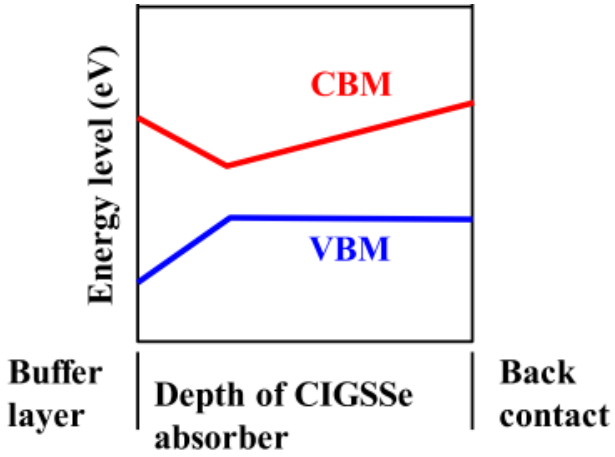




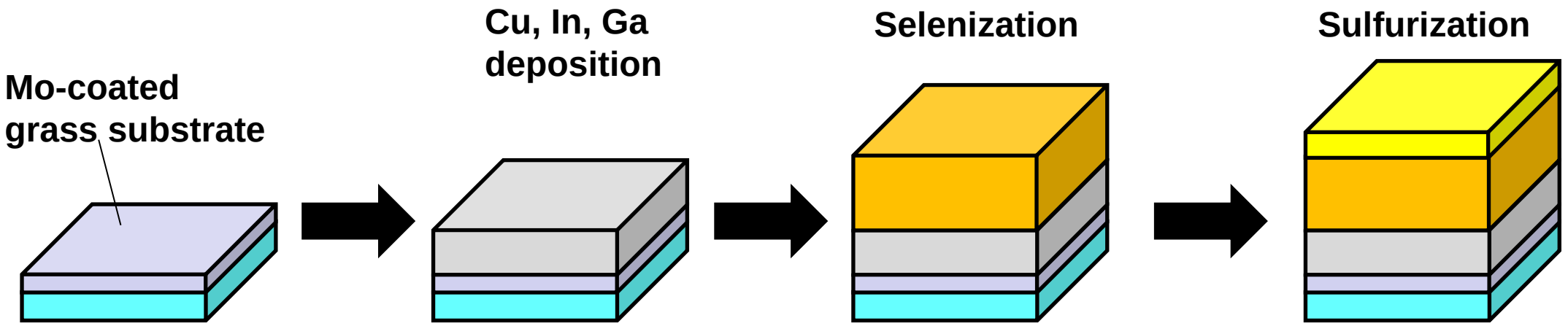


A double graded band profile is formed due to gradient of Ga/(Ga+In) and S/(S+Se) ratios in CIGSSe absorber layer.

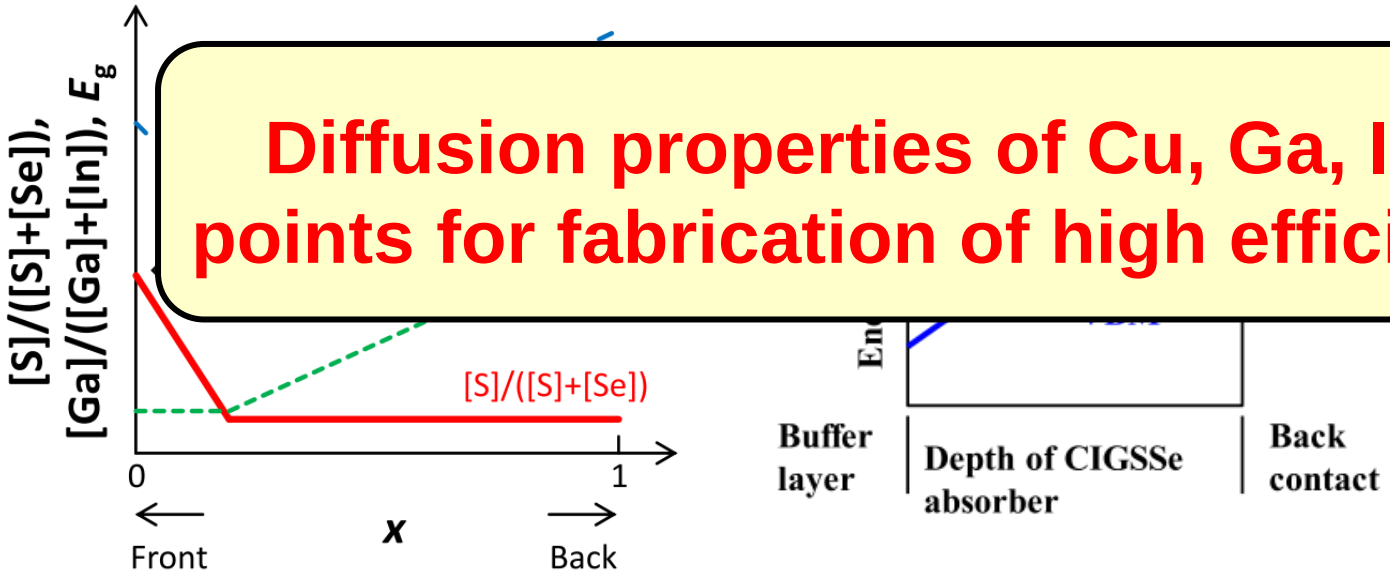
T. Kato, Jpn. J. Appl, Appl. Phys., 56, 04CA02 (2017). T. Maeda *et al.*, Jpn. J. Appl, Appl. Phys., 59, SGGF12 (2020).

Fabrication method of $Cu(In,Ga)(S,Se)_2$ films

- **Sulfurization after selenization process**



Diffusion properties of Cu, Ga, In and S atoms are key-points for fabrication of high efficiency CIGSSe solar cells.



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T. Kato, Jpn. J. Appl, Appl. Phys., 56, 04CA02 (2017). T. Maeda *et al.*, Jpn. J. Appl, Appl. Phys., 59, SGGF12 (2020).

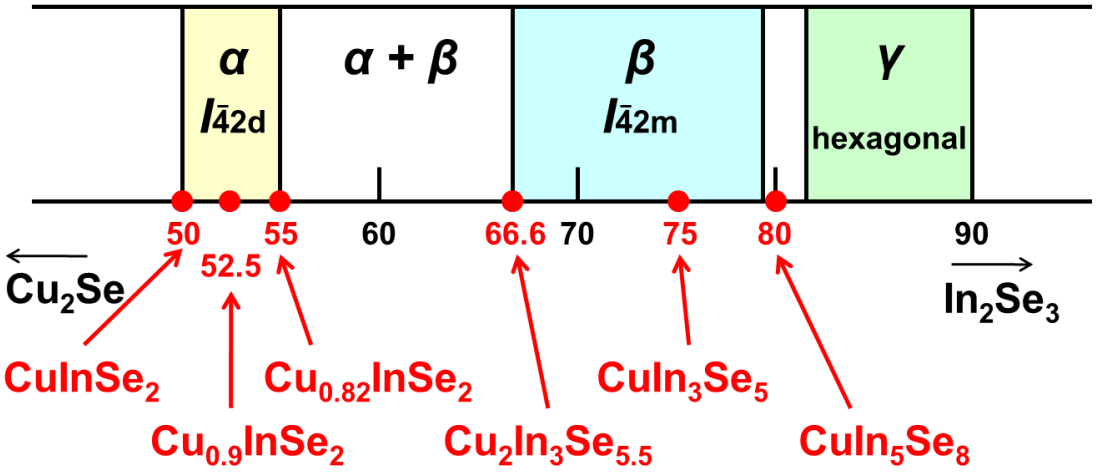
XAFS analysis for CIS and related materials

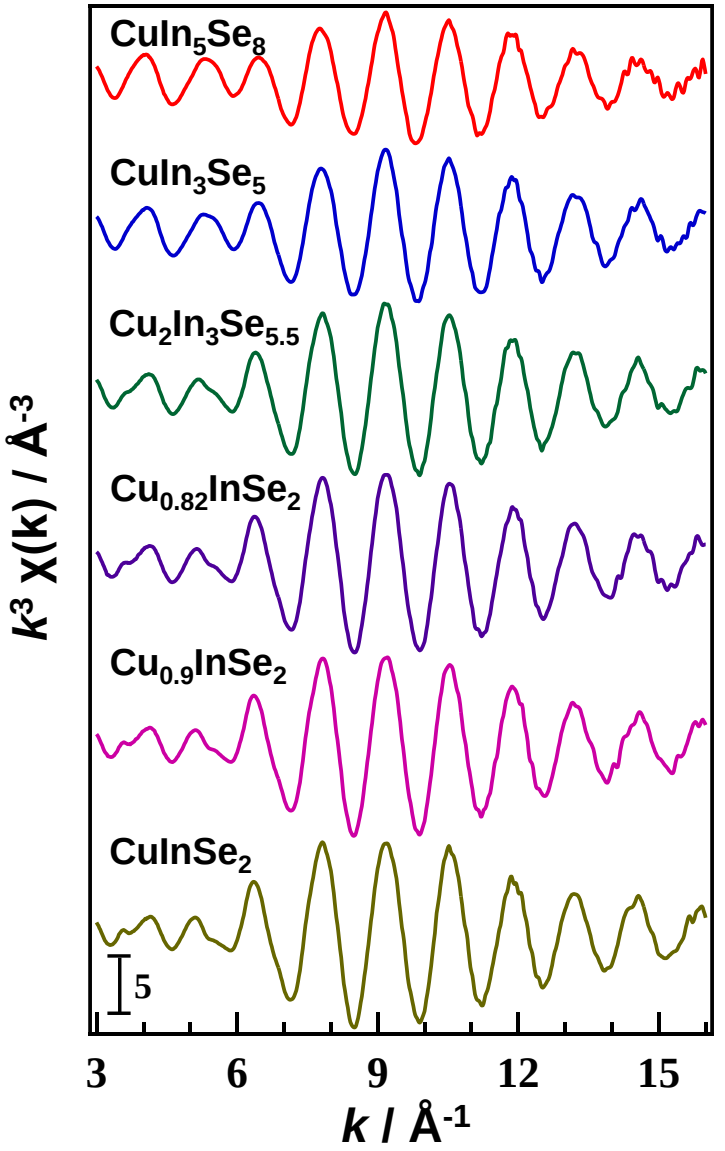
A structural study of Cu-In-Se compounds by x-ray absorption fine structure

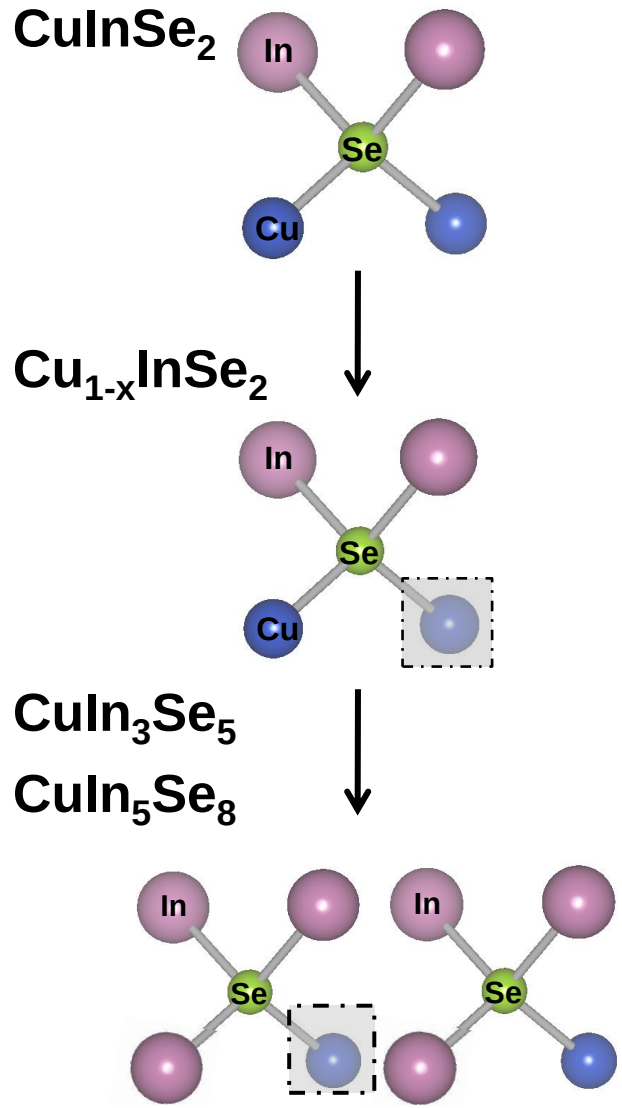
S. Yamazoe, H. Kou, T. Wada

J. Mater, Res., 26, 1504 (2011).

The local structures about Cu, In, and Se atoms in a series of Cu_2Se–In_2Se_3 pseudobinary compounds have been investigated by XAFS. We conclude that $Cu_{0.9}InSe_{1.95}$ and $Cu_{0.82}InSe_{1.91}$ have a chalcopyrite structure with V_{Cu} and that the structure of $CuIn_3Se_5$ and $CuIn_5Se_8$ is a stannite-like structure with V_{Cu} and In_{Cu} defects.

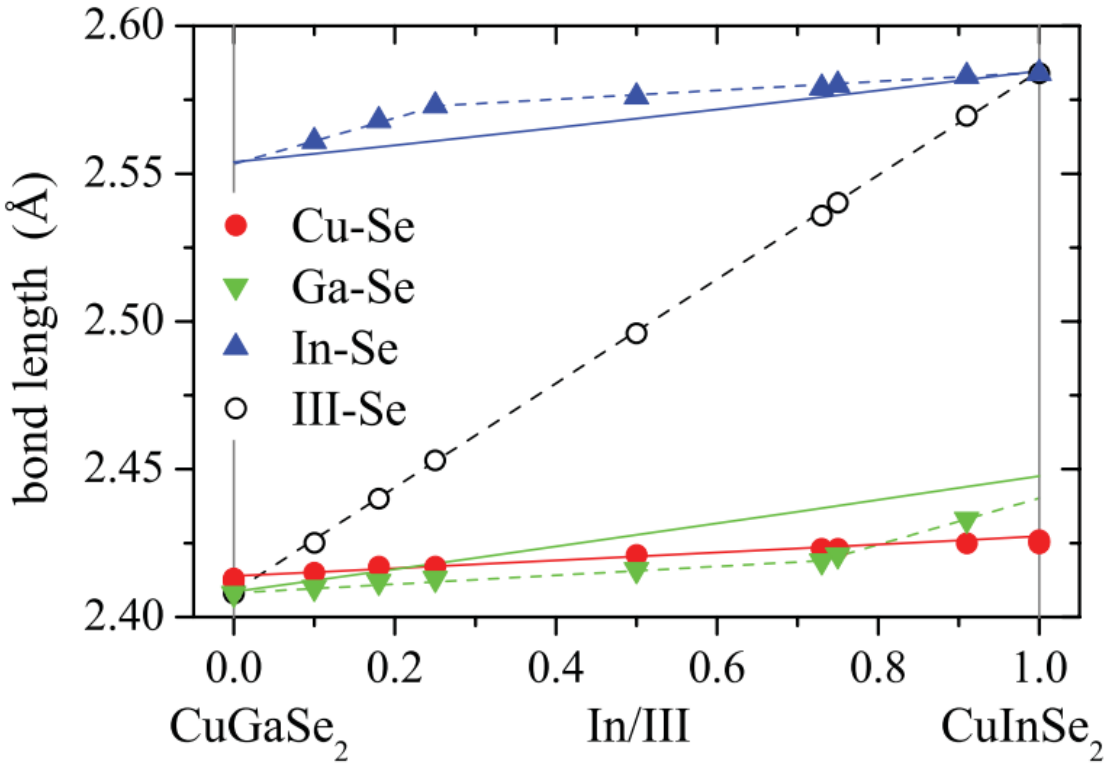


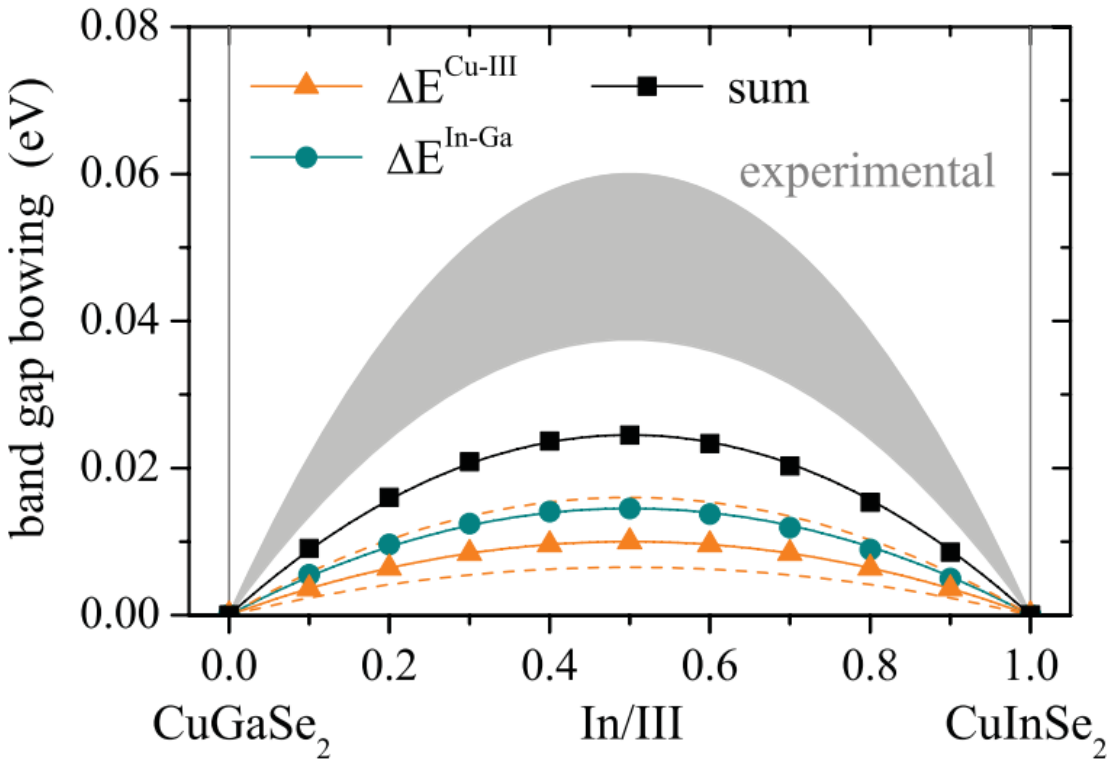




Low-temperature XAFS

- **Precise structural analysis**





C.S. Schnohr et al., Phys. Rev. B, 85, 245204 (2012).

Low-temperature XAFS measurement gives local atomic arrangement significantly differed from average crystallographic structure obtained by x-ray or neutron diffraction.

Low-temperature XAFS

- **Evaluation for property of chemical bond**

EXAFS equation

$$\chi(k) = S_0^2 \sum \frac{CN}{kr^2} f(k;\pi) \exp(-2\sigma^2 k^2) \sin(2kr + \delta(k) - \frac{4}{3} C_3 k^3)$$

Low-temperature XAFS

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Einstein model

Interatomic vibration is treated as a harmonic oscillator.

Einstein frequency of chemical bond

$$\omega_E = \frac{2\pi k_B \theta_E}{h}$$

h : Planck constant

k_B : Boltzmann constant

θ_E : Einstein temperature

Low-temperature XAFS

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Einstein temperature is determined by following equation.

$$\sigma^2 = \sigma_S^2 + \frac{h^2}{8\pi^2 \mu k_B \theta_E} \coth\left(\frac{\theta_E}{2T}\right)$$

μ : Reduced mass

T : Temperature

Low-temperature XAFS

- **Evaluation for property of chemical bond**

EXAFS equation

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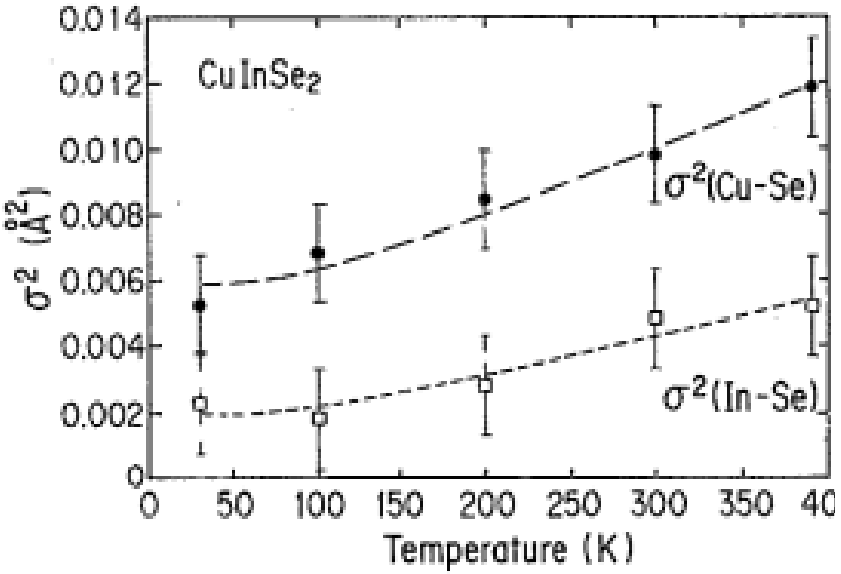
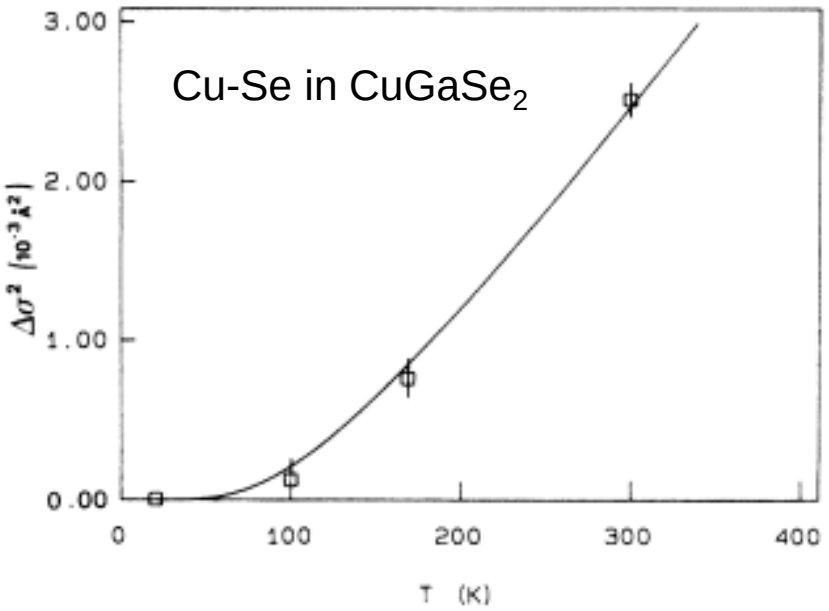
Evaluation using Einstein temperature is expected to be the evaluation of diffusion property of the chemical species.

Low-temperature XAFS

- **Evaluation for chemical bonds in $CuInSe_2$ and $CuGaSe_2$**



*Y. Kuwahara et al., J. Appl. Phys., 76, 7864 (1994).



**P.P. Lottici et al., Phys. Rev. B, 37, 9017 (1988).

	Einstein Temperature / K		
	Cu-Se	In-Se	Ga-Se
*$CuInSe_2$	251	283	-
**$CuGaSe_2$	309	-	345

Studies on Evaluation of chemical bonds in CIGSe and CIGS are limited. We performed the chemical bond analysis of CIGSe and CIGS series using low-temperature XAFS.

Experimental

Sample Preparation

$Cu(In,Ga)Se_2$ and $Cu(In,Ga)S_2$

Weighing ← Elemental powders were weighed to objective composition.

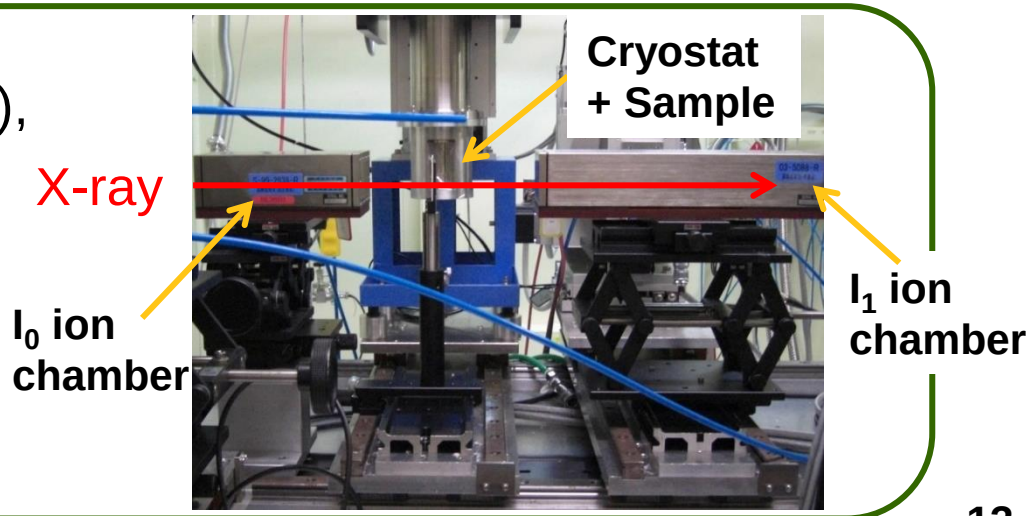
Mixing ← By using planetary ball milling under N_2 atmosphere.

Heating ← 550 ºC for 30 min under N_2 atmosphere

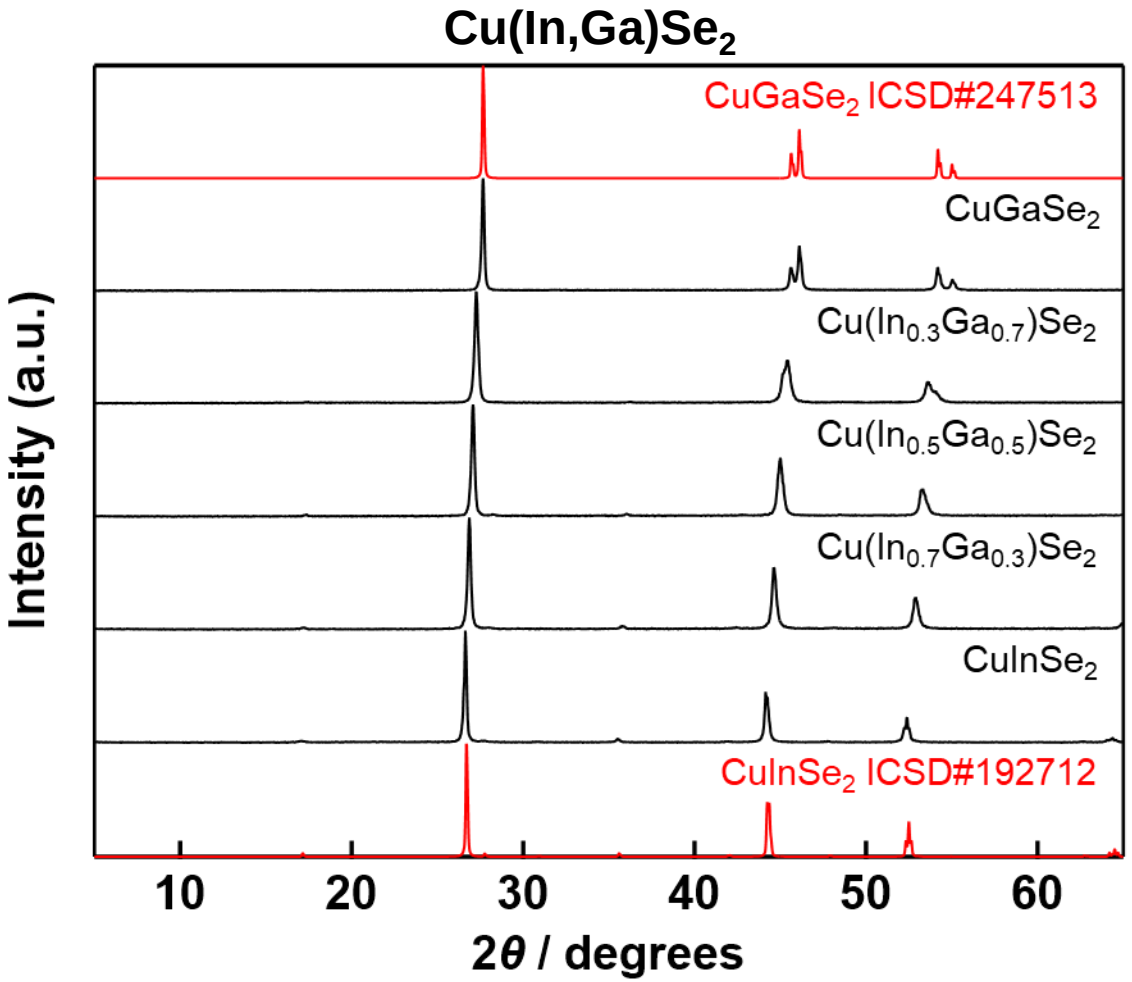
XAFS measurement

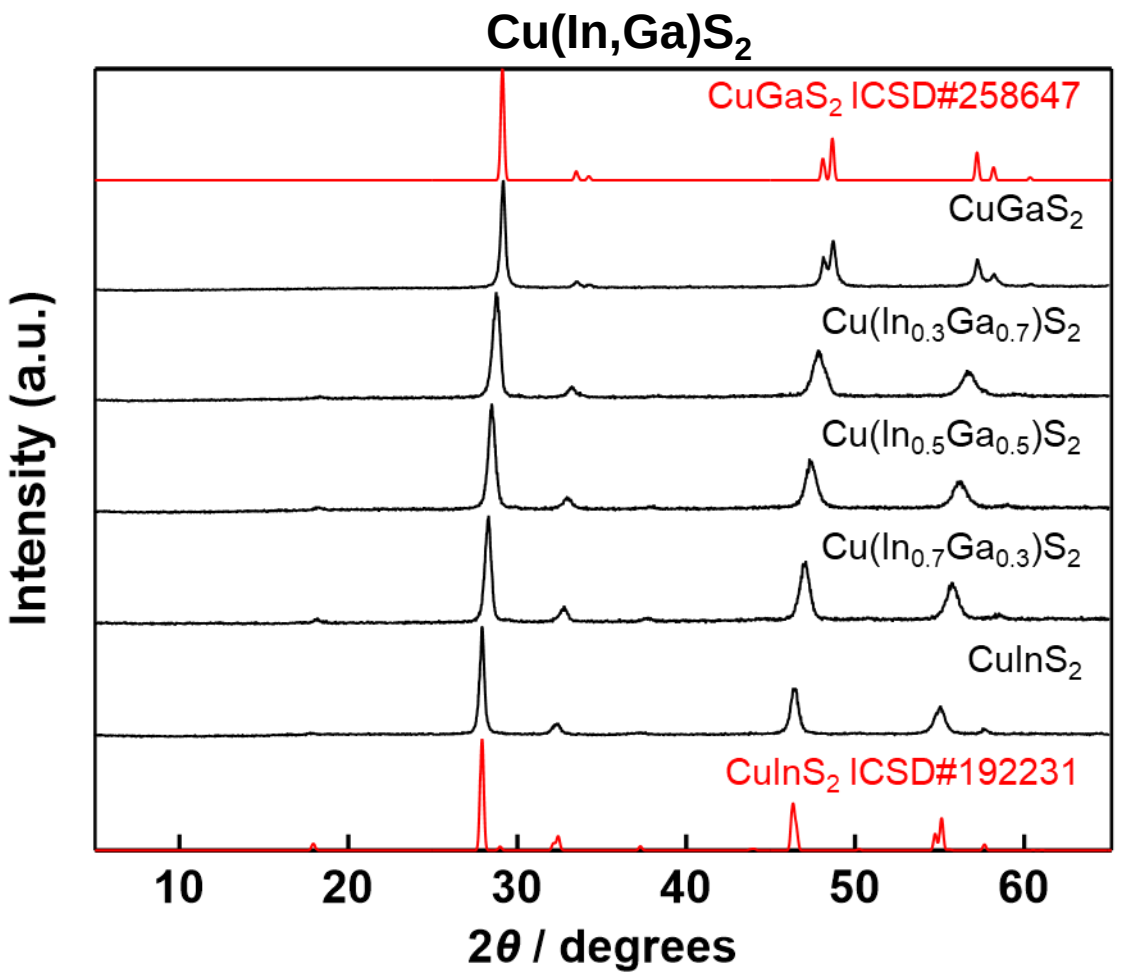
The powder samples was diluted by boron nitride (BN), and pressed and molded into a disc shape.

XAFS spectra (Cu, In, Ga K-edge) were recorded in transmission mode at 10, 20, 50, 100, 200 and 300 K using a Si(311) double crystal monochromator at SPring-8 BL01B1.



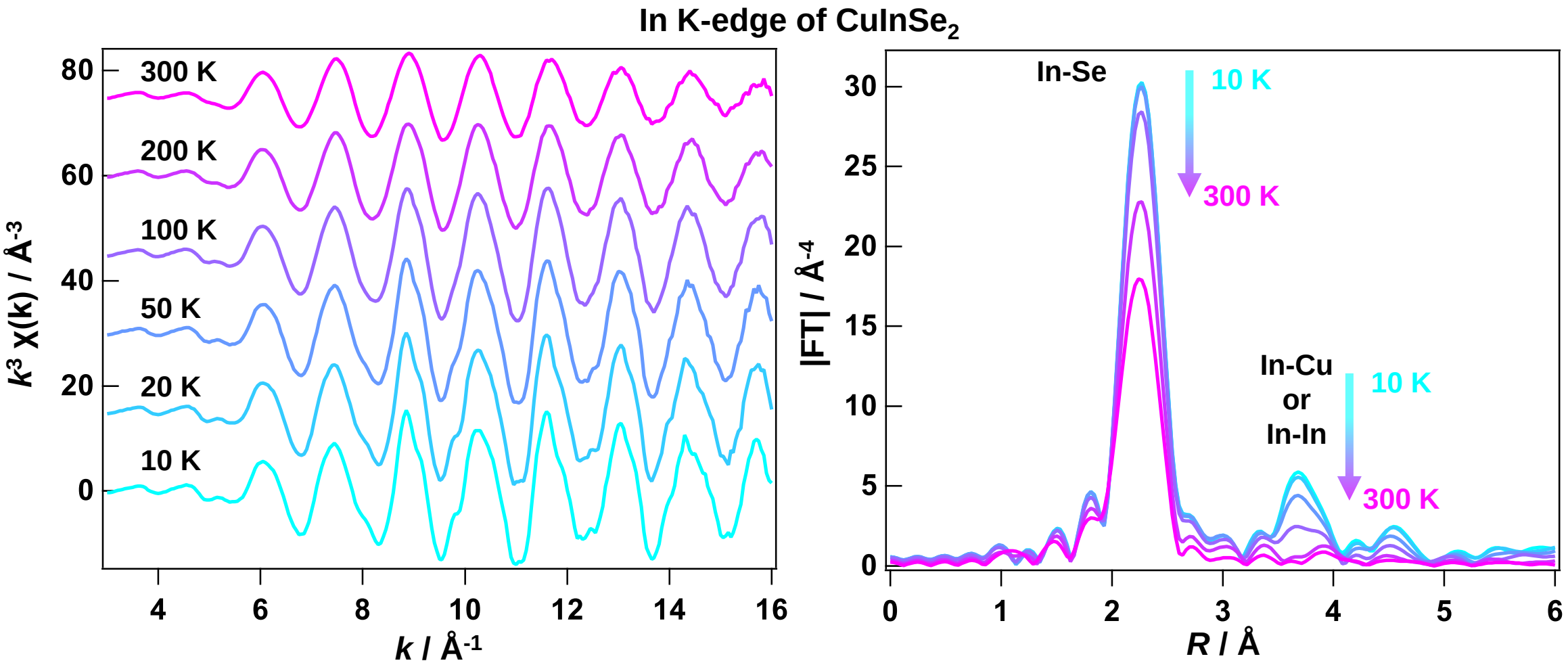
XRD patterns





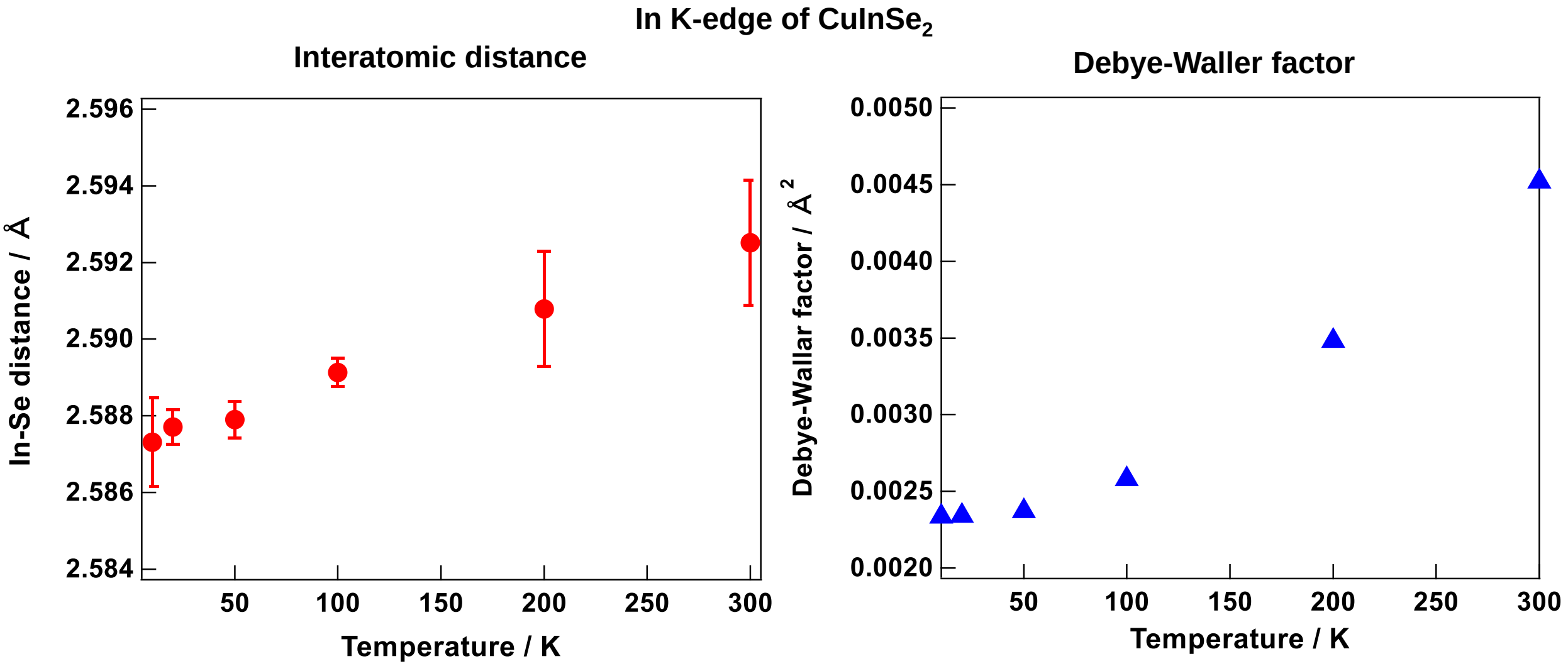
Cu(In,Ga)Se_2 and Cu(In,Ga)S_2 with chalcopyrite-type structure were successfully synthesized.

Temperature dependence of EXAFS



The EXAFS oscillation got closer to a monotonous sine function with increasing temperature.
The peak in the second coordination sphere disappeared with increasing temperature.

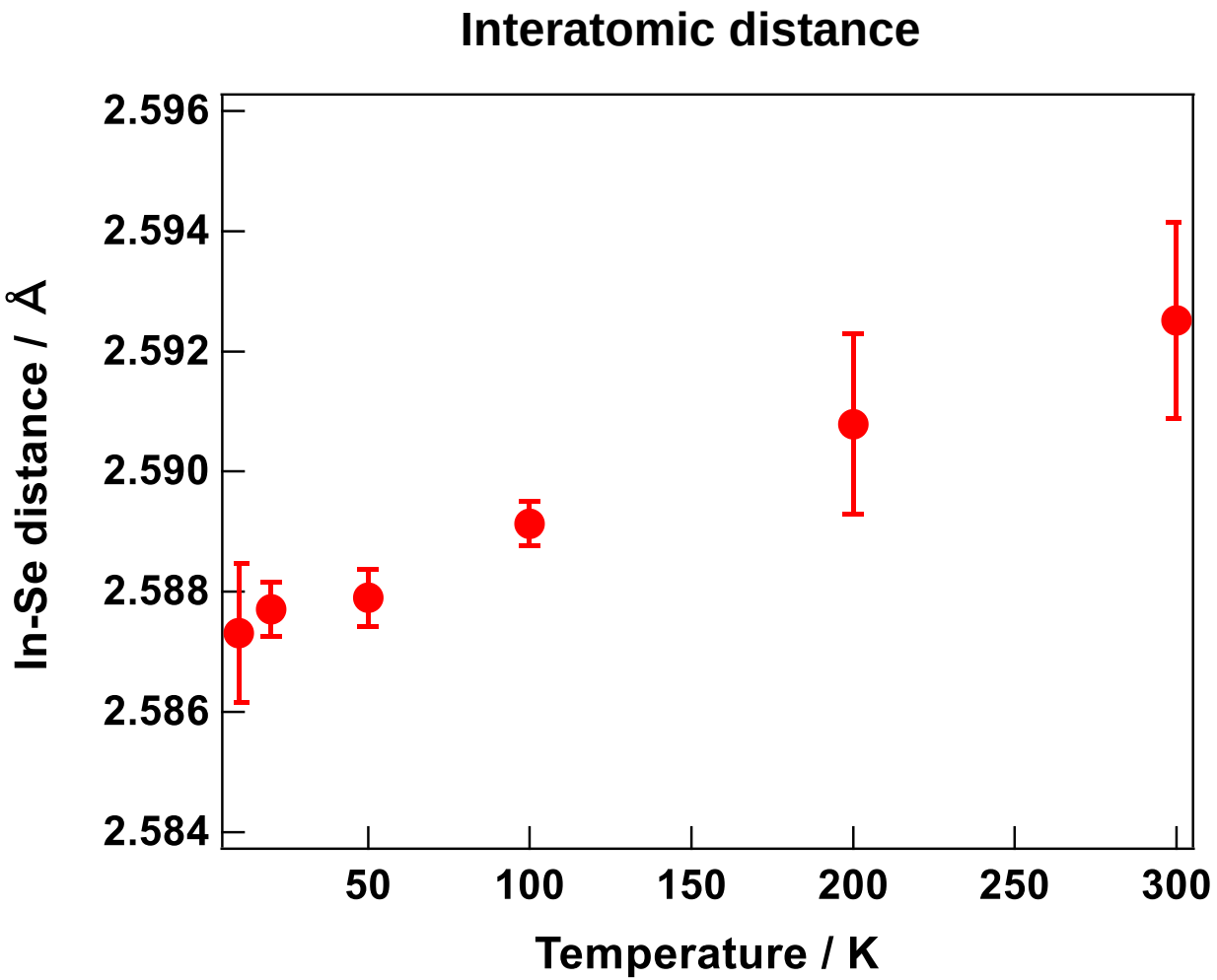
Temperature dependence

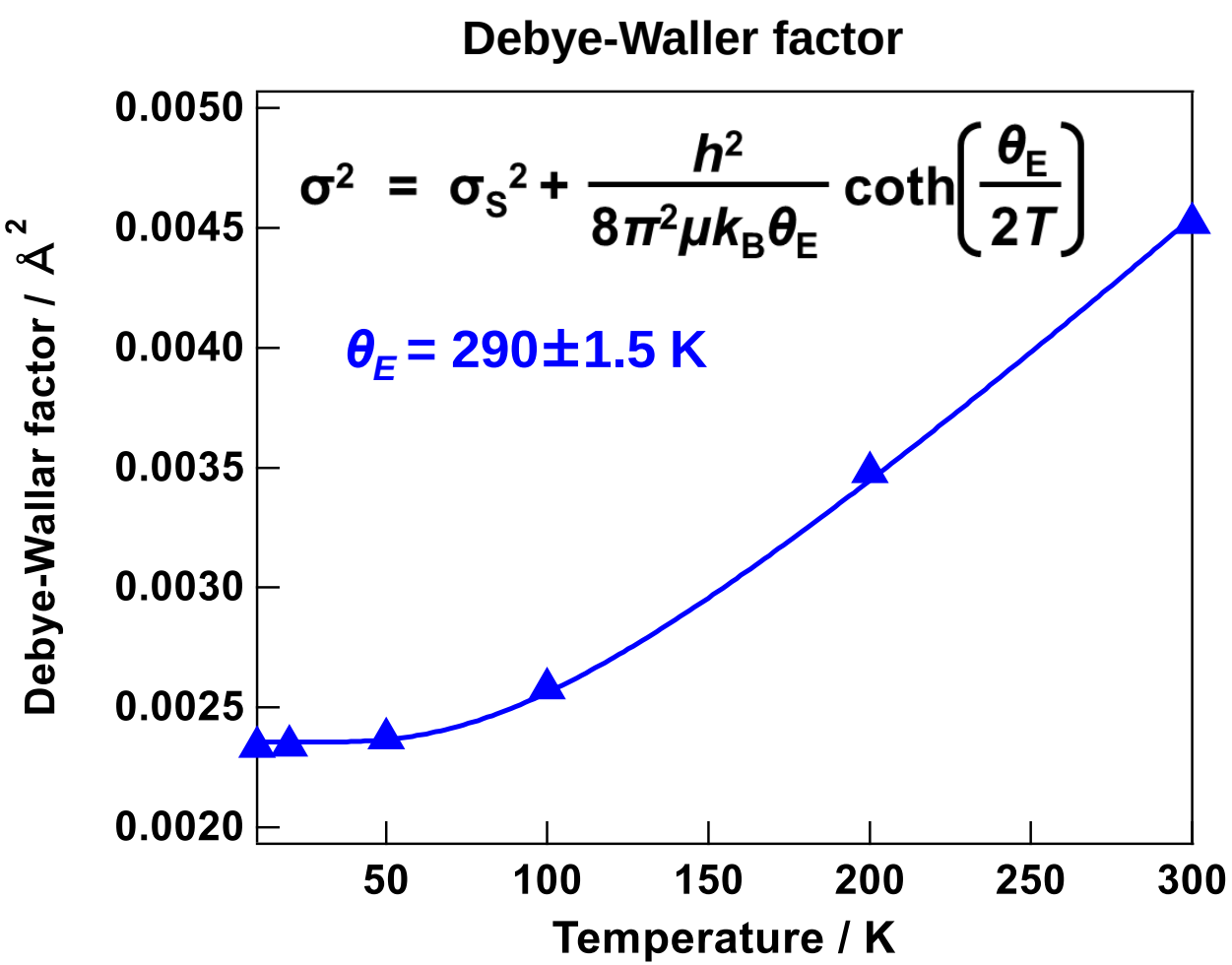


The bond length and Debye-Waller factors increased with temperature.

Temperature dependence

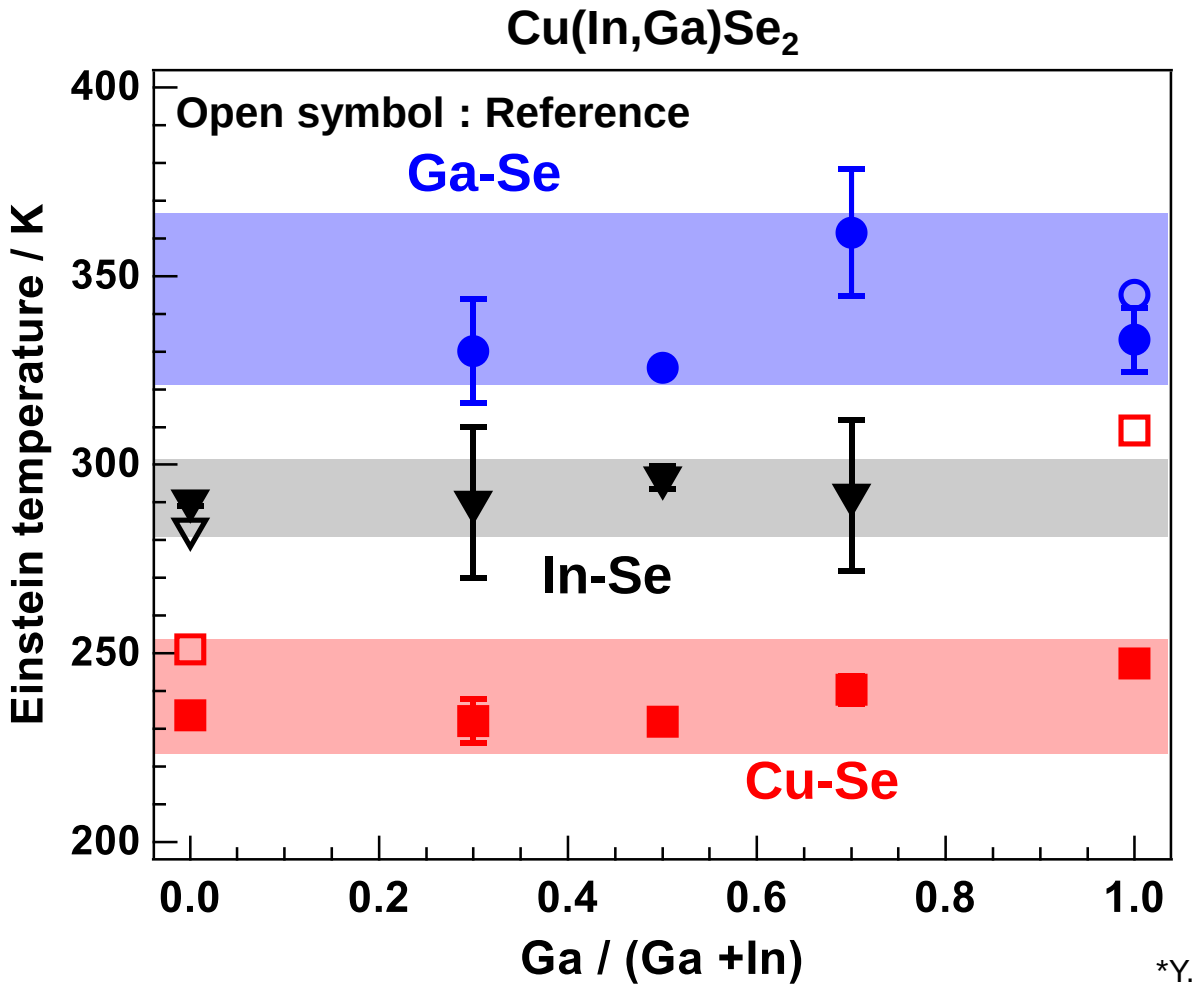
In K-edge of $CuInSe_2$





Einstein temperature of In-Se bond in $CuInSe_2$ was determined by temperature dependence of Debye-Waller factors.

Einstein temperature



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**P.P. Lottici et al., Phys. Rev. B, 37, 9017 (1988).

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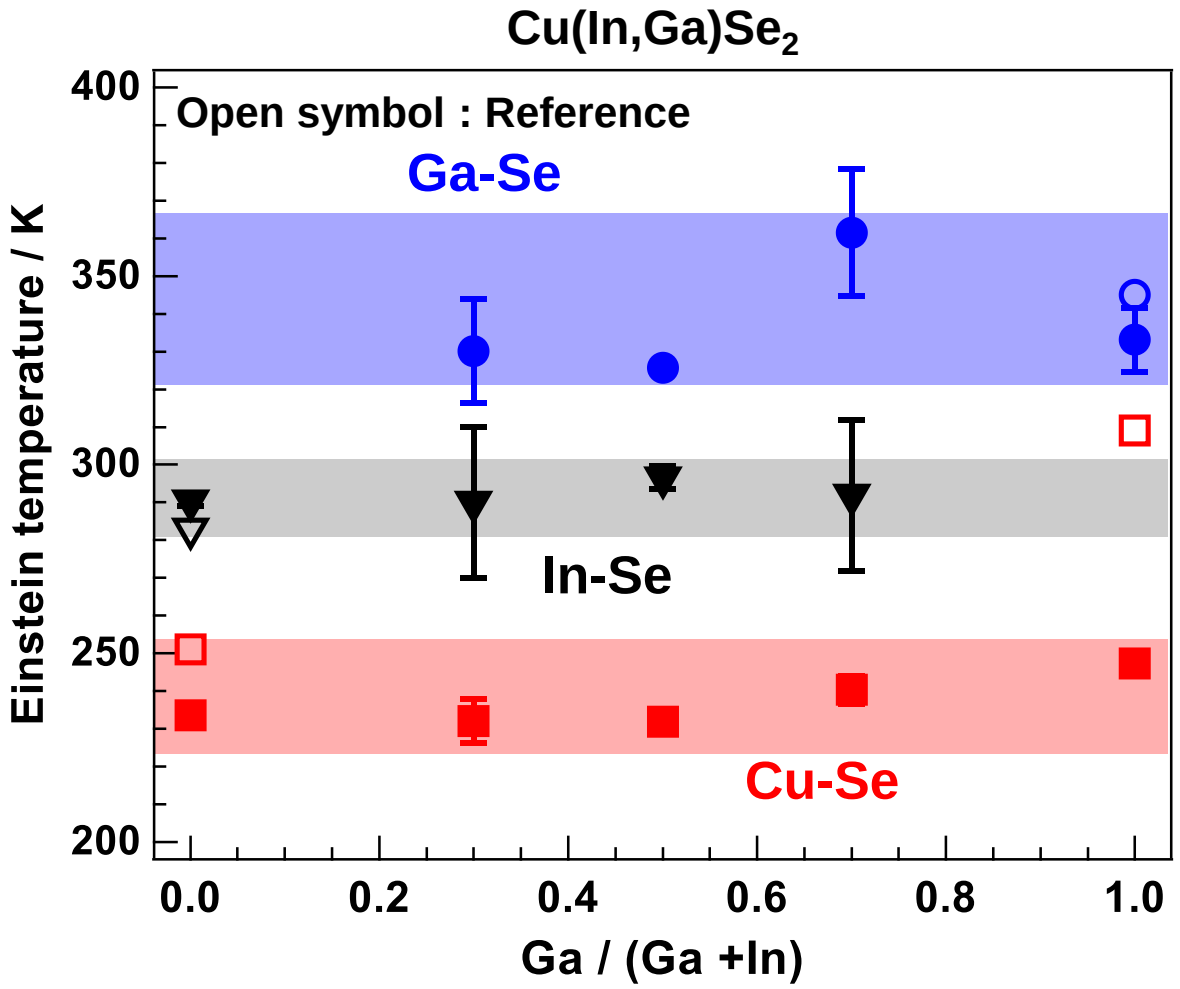


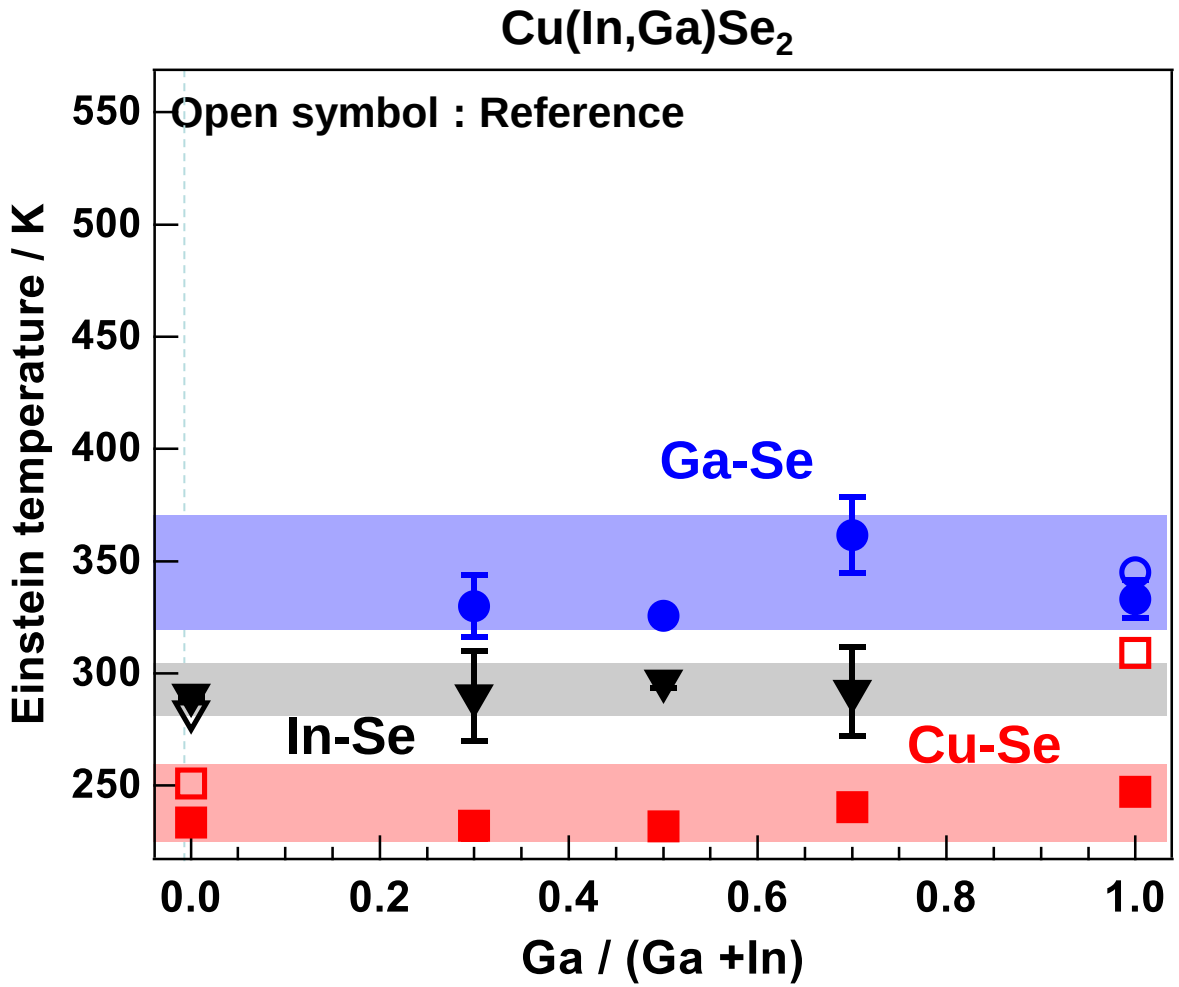
Activation energy of migration			
	Cu	In	Ga
$CuInSe_2$	1.06 eV	1.70 eV	-
$CuGaSe_2$	0.94 eV	-	1.89 eV

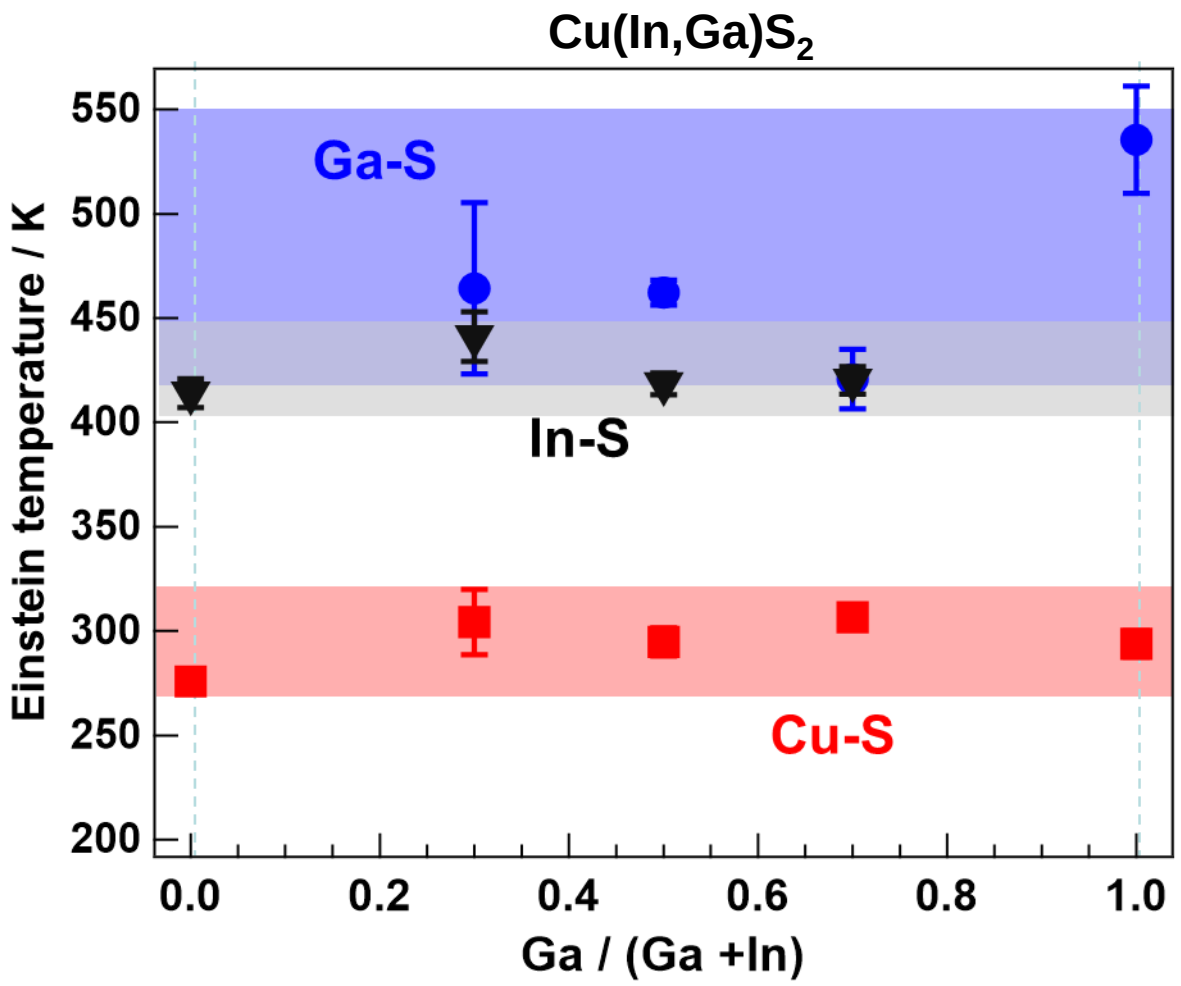
S. Nakamura et al., Jpn. J. Appl, Appl. Phys., 52, 04CR01 (2013).

S. Nakamura et al., Phys. Status. Solidi. A, 210, 1317 (2013).

The evaluation of the bond hardness by Einstein temperature is consistent with the trend of the theoretical calculations.

Einstein temperature



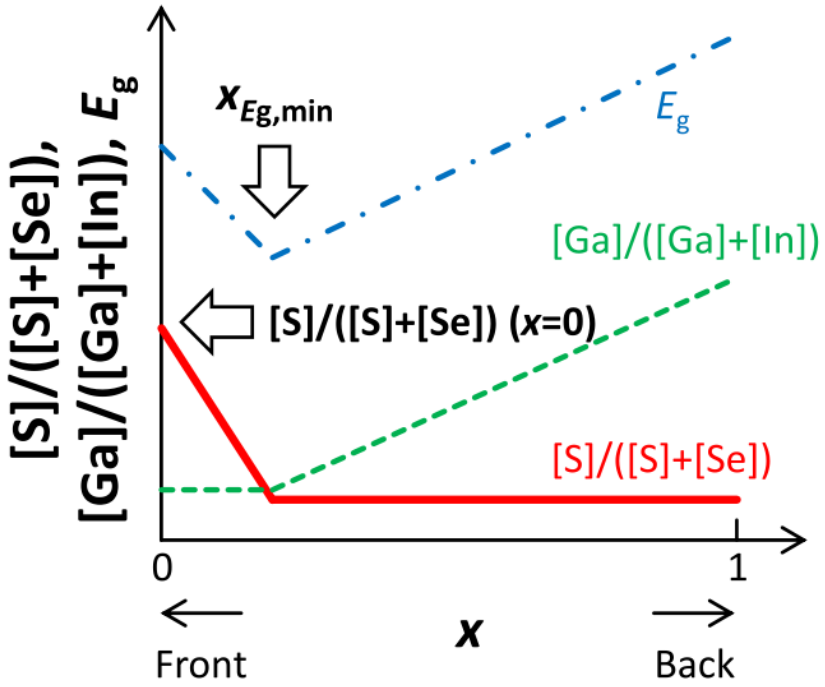


Comparing the $Cu(In,Ga)Se_2$ and $Cu(In,Ga)S_2$ systems, the Einstein temperature of the bonds in $Cu(In,Ga)S_2$ is clearly higher.
→The bonds are hard.

Conclusion

- **Evaluation of chemical bonds in CIGSe and CIGS using low-temperature XAFS was performed.**

- **The results of the analysis using the Einstein model are applicable to the evaluation of diffusion.**



- **For $Cu(In,Ga)Se_2$ and $Cu(In,Ga)S_2$, the order of bond hardness is Ga-Se(S) > In-Se (S) > Cu-Se (S).**

- **The bonds in $Cu(In,Ga)S_2$ are harder than those bonds in $Cu(In,Ga)Se_2$. The result indicates that sulfur is more difficult to diffuse in $Cu(In,Ga)(S,Se)_2$ than selenium.**

T. Kato, Jpn. J. Appl, Appl. Phys., 56, 04CA02 (2017).