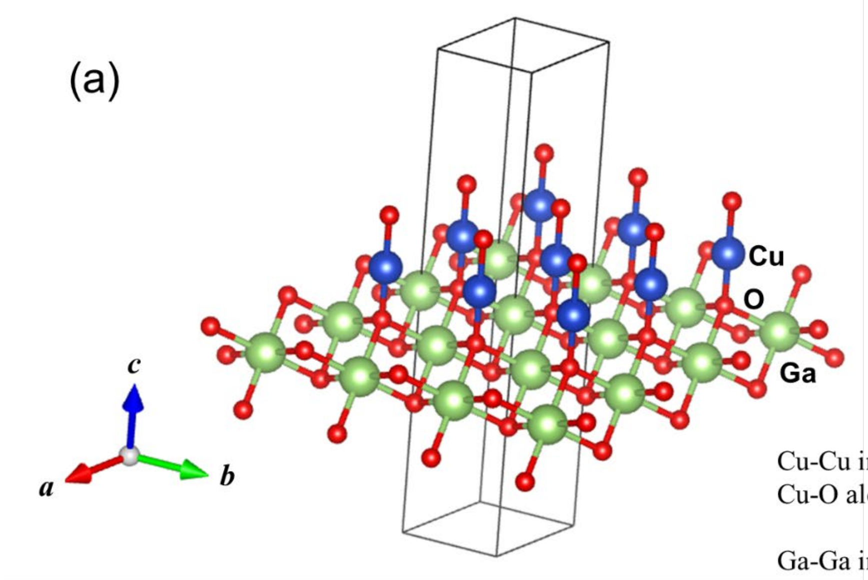
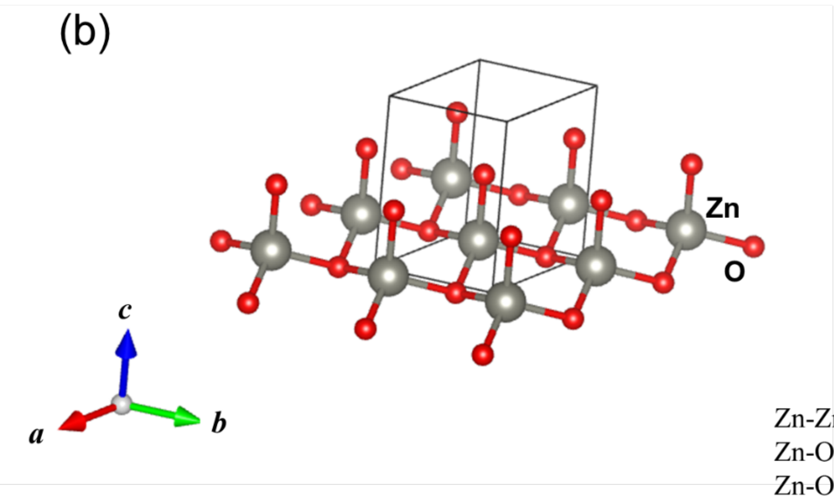


Cu-Cu in *a*-*b* plane: 2.9770(10) Å
Cu-O along with *c*-axis: 1.84710 Å

Ga-Ga in *a*-*b* plane: 2.9770(10) Å
Ga-O in GaO_6 octahedron: 1.9957(5) Å

Figure S1. (a) Extracted crystal structure of rhombohedral $CuGaO_2$ (*R*-3*m*). Blue, red, and green balls show Cu, O, Ga elements, respectively. The lattice parameters are taken from ICDD PDF 01-082-8561.

Figure S1(a) shows crystal structure in part of rhombohedral $CuGaO_2$ (*R*-3*m*). The closest distance of Cu-Cu found in a-b plane is 2.9770(10)Å and one of Cu-O is 1.84710 Å along with the c-axis. On the other hand, the closest distance of Ga-Ga is 2.9770(10) Å and the Ga-O distance in GaO_6 octahedron is 1.9957(5) Å. It is also seen that oxygen has fourfold coordination with one Cu and three Ga. Cu is combined with two oxygens along with the *c*-axis and Ga has six-fold coordination with oxygens.



Zn-Zn in *a*-*b* plane: 3.25010(11) Å
Zn-O along with *c*-axis: 1.98755 Å
Zn-O with other three oxygens: 1.97497(6) Å

Figure S1. (b) Extracted crystal structure of wurtzite(hexagonal) ZnO ($P6_3mc$). Grey and red balls show Zn and O elements, respectively. The lattice parameters are taken from ICDD PDF 04-003-2106.

As for ZnO shown in **Figure S1(b)**, the closest distance of Zn-Zn found in *a*-*b* plane is 3.25010(11) Å. The Zn-O distance along with the *c*-axis is 1.97497(6) Å, which Zn element has bonds with the other three oxygen in a length of 1.98755(4). As it is well known, Zn has fourfold coordination with oxygens and O has four neighboring Zn elements within a distance < 1.99 Å.

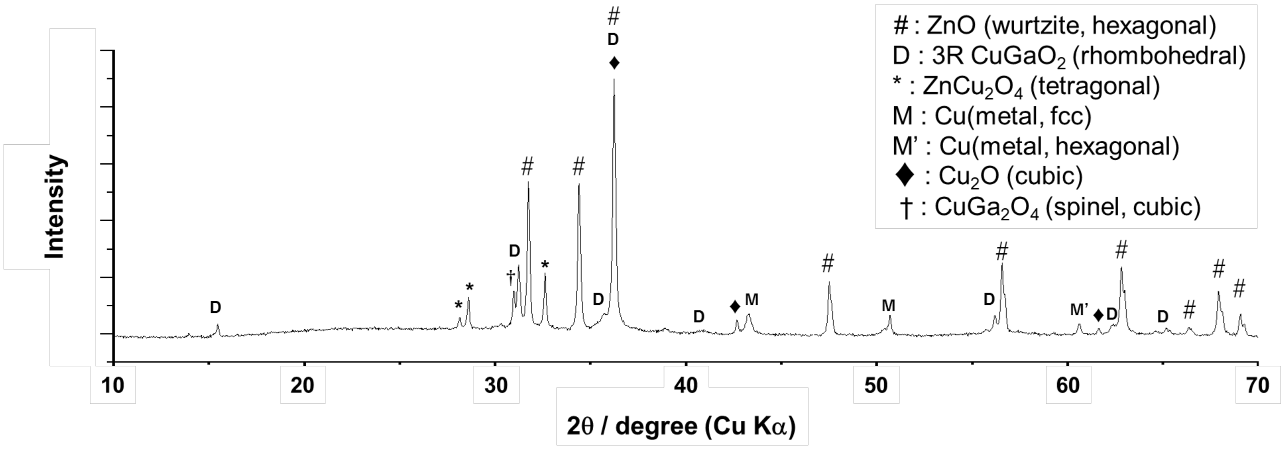


Figure S2. XRD pattern of CZ3 sample (after the H_2 annealing process) and assignment of the corresponding crystals.

Table S1. XRD peak assignment for the CZ3 sample

No.	XRD peak position	Assignment (*h k l*)					
		$CuGaO_2$, rhombohedral	ZnO, hexagonal	$CuGa_2O_4$, cubic	$ZnCu_2O_4$, tetragonal	Cu_2O, cubic	Cu(fcc), fcc or hexa
1	13.961	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	15.465	0 0 3					
3	28.132				1 1 2		
4	28.600				1 0 3		
5	30.970			2 2 0			
6	31.240	0 0 6					
7	31.741		1 0 0				
8	32.610						
9	34.382		0 0 2				
10	35.752	1 0 1					
11	36.220	0 1 2	1 0 1			1 1 1	
12	40.866	1 0 4					
13	42.671					2 0 0	
14	43.306						1 1 1 (fcc)
15	47.517		1 0 2				
16	50.692						2 0 0 (fcc)
17	56.173	0 1 8					
18	56.574		1 1 0				
19	60.618						1 0 4 (hexa)
20	61.621					2 2 0	
21	62.390	1 1 0					
22	62.824		1 0 3				
23	65.164	1 0 10					
24	66.334		2 0 0				
25	67.905		1 1 2				
26	69.074		2 0 1				

n.a.: not assigned

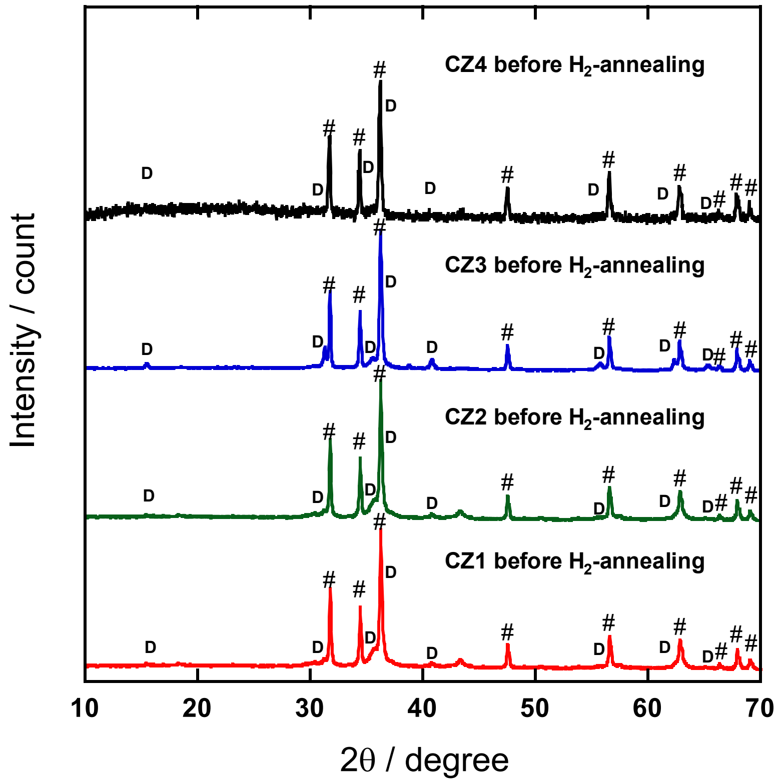


Figure S3. XRD patterns of $CuGaO_2$/ZnO hybrids of CZ1-4 before the H_2 annealing process. (#:wurtzite ZnO, D:rhombohedral(3R) $CuGaO_2$).

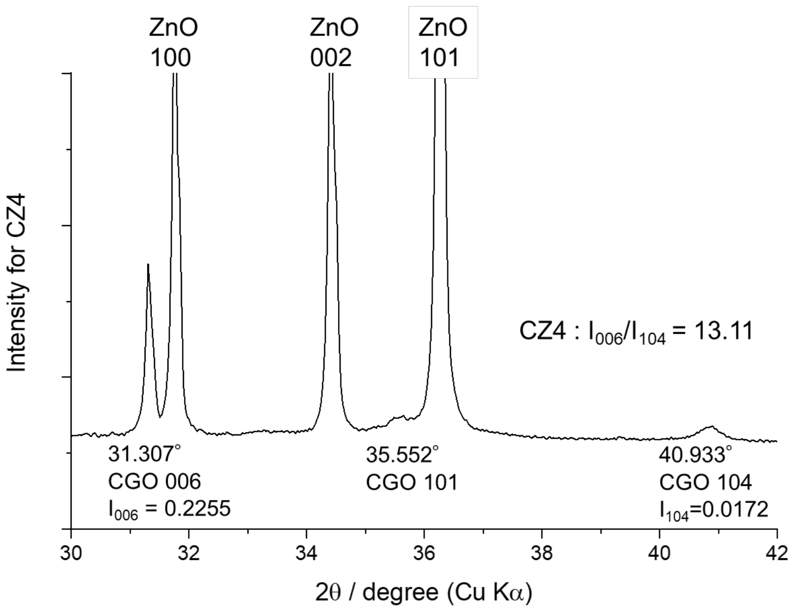


Figure S4. XRD pattern (magnified) of CZ4 sample after the H_2 annealing process.

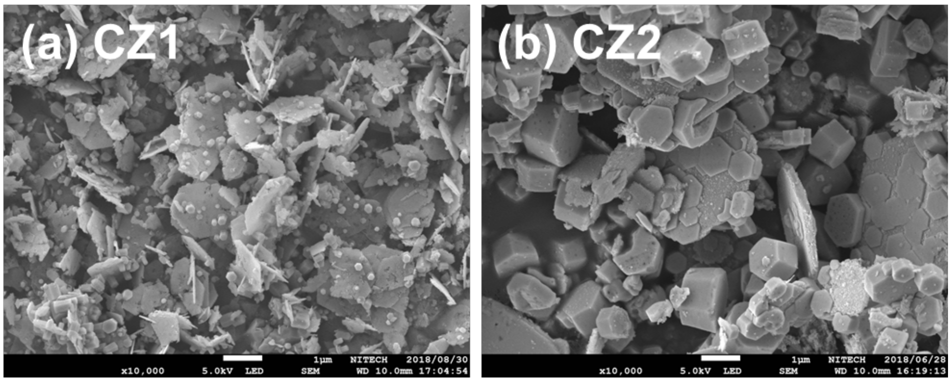


Figure S5. SEM images of the CZ1 (a) and CZ2 (b) samples.

As seen in **Figure S5(a,b)**, in CZ1 with a nominal [Zn]/[Cu] ratio of 2.75, granular ZnO is observed on $CuGaO_2$ particles of 2 μm, while CZ2 ([Zn]/[Cu] = 5.5) shows a layer of ZnO on the surface of $CuGaO_2$ particles larger than 2 μm, and rod-shaped ZnO particles are distinct without the formation of $CuGaO_2$/ZnO hybrids. By increasing the amount of $Zn(CH_3COO)_2 \cdot 2H_2O$, it is more likely to achieve a complete coverage of $CuGaO_2$ hexagonal plates with a ZnO layer.

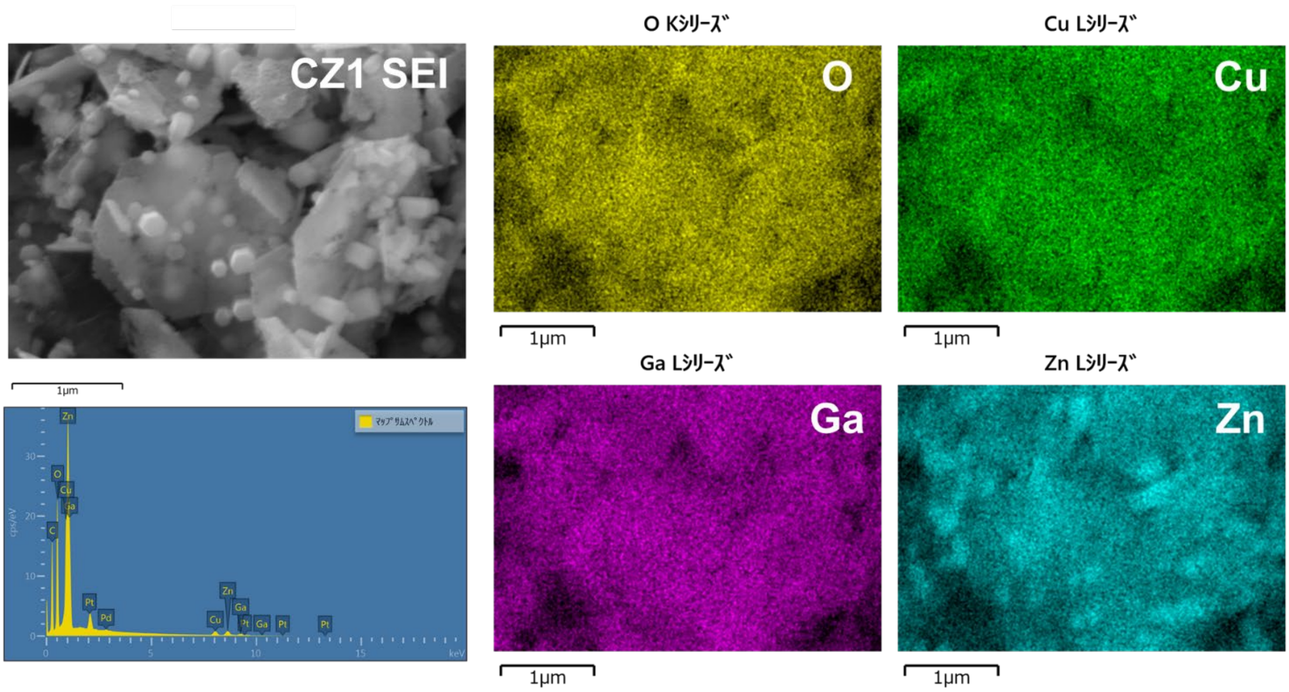


Figure S6. SEM-EDS results of the CZ1 sample.

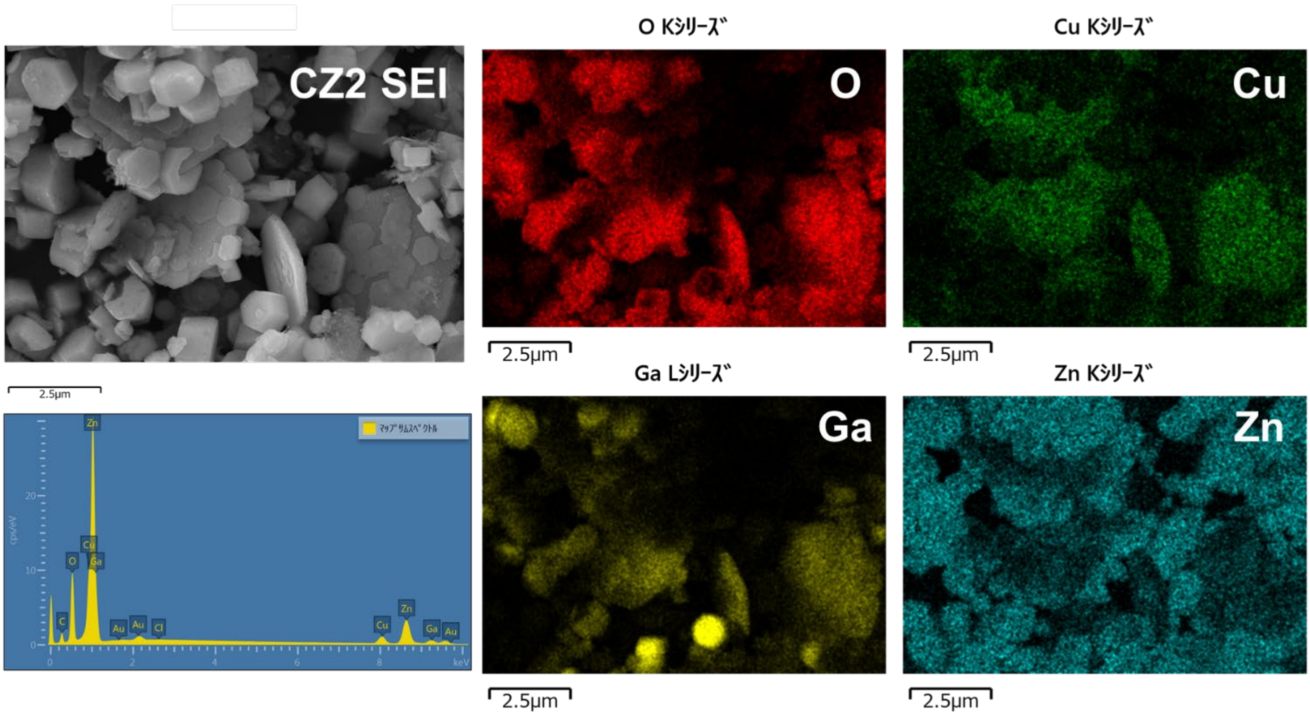


Figure S7. SEM-EDS results of the CZ2 sample.

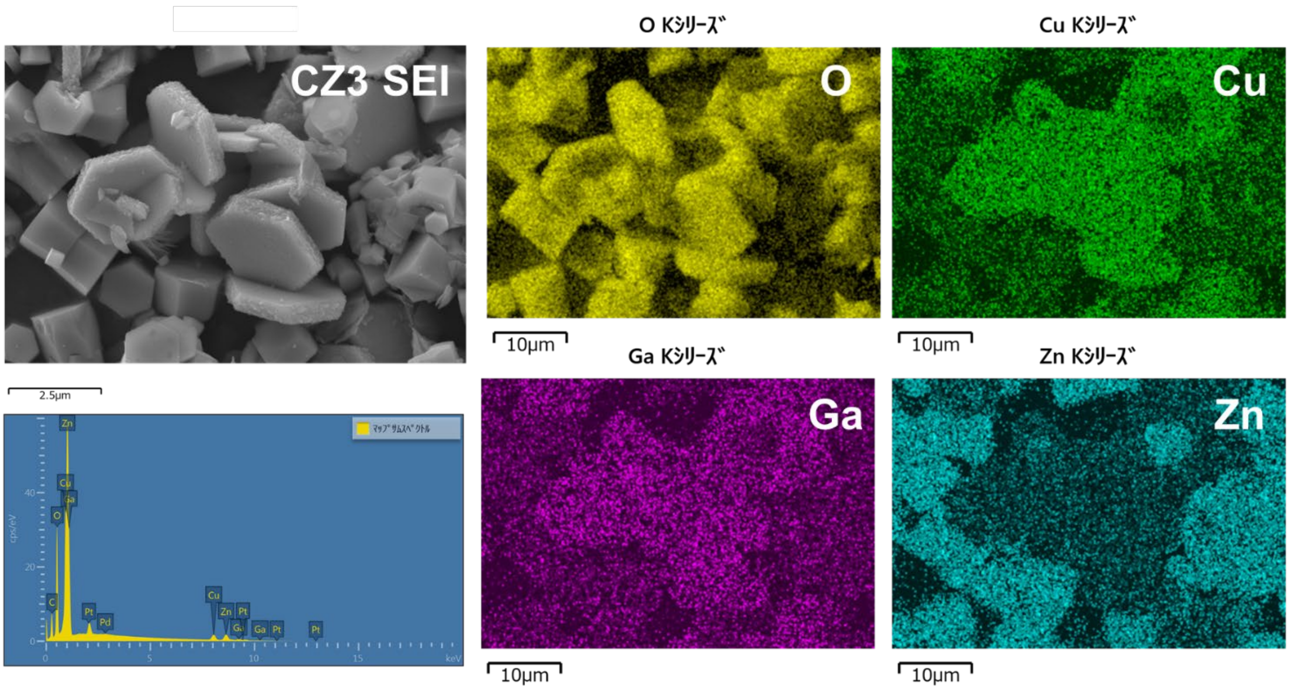


Figure S8. SEM-EDS results of the CZ3 sample.

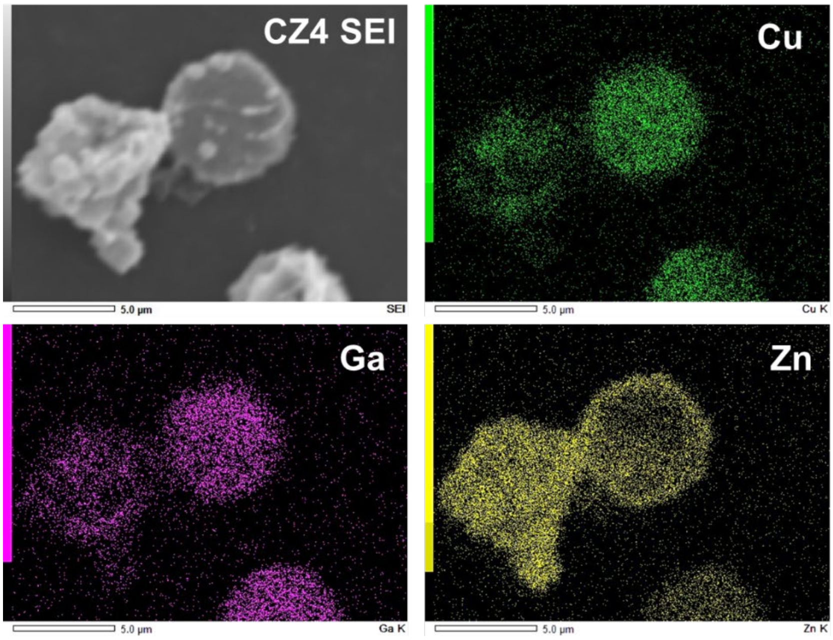


Figure S9. SEM-EDS results of the CZ4 sample, which are taken, for comparison with **Fig.S5-7**, from the literature (M. Choi, S. Yagi, Y. Ohta, K. Kido and T. Hayakawa, *J. Phys. Chem. Solids,* 150 (2021) 109845).

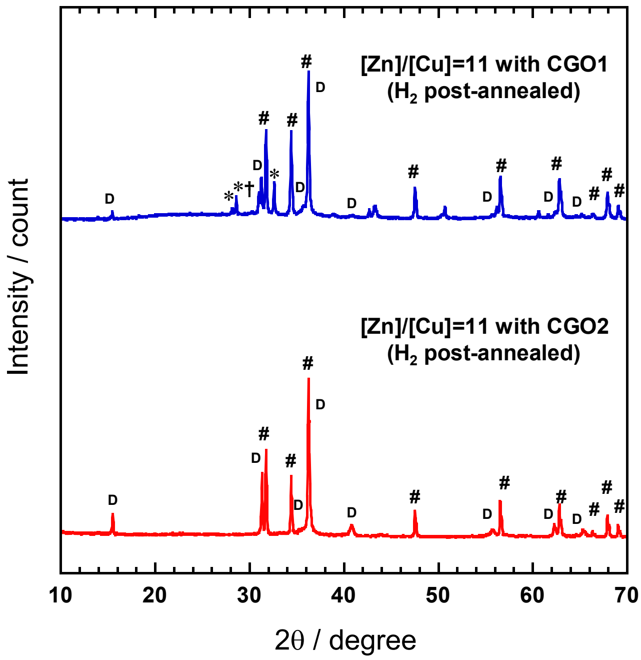


Figure S10. Comparison of XRD patterns for two $CuGaO_2$/ZnO hybris synthesized with the same [Zn]/[Cu] ratio (=11) but by use of the different base crystals, CGO1 and CGO2 (#:wurtzite ZnO, D:rhombohedral(3R) $CuGaO_2$). Both the hybrids were annealed in the H_2 atmosphere. The CGO1 particles used were mainly 1~3 μm in size, while the CGO2 particles with the size bigger than 3 μm, typically 5~8 μm were obtained, meaning that the specific surface area (SSA) of the particles of CGO1 was higher, and thus that more oxygen molecules would possibly be adsorbed on CGO1, which make it more likely that the partial decomposition to CuO and Ga_2O_3 took place on CGO1. This would make it possible to form the $ZnCu_2O_4$ and $CuGa_2O_4$ in CZ3 by **Reactions 1 and 2** given in the maintext.

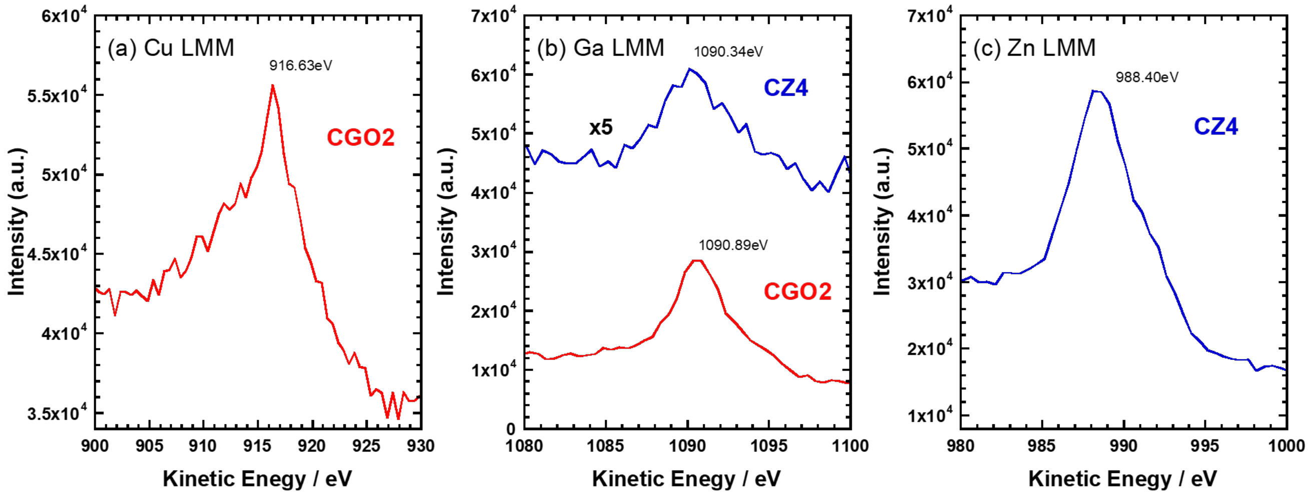


Figure S11. Auger $L_3M_{4,5}M_{4,5}$ spectra for CGO2 ((a)Cu LMM and (b) Ga LMM) and CZ4 ((b) Ga LMM and (c) Zn LMM).

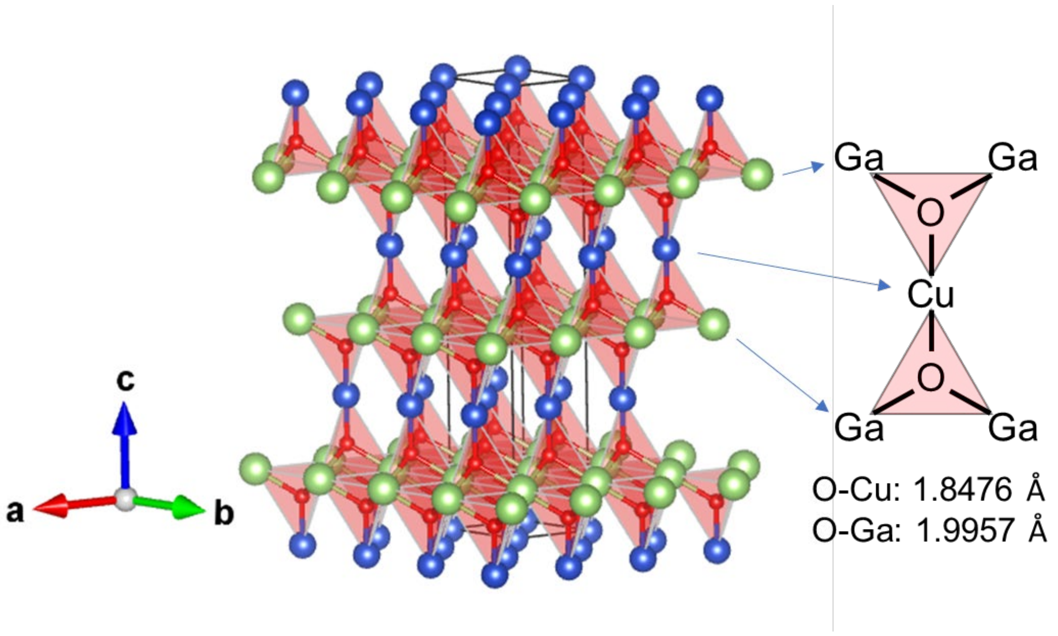


Figure S12. Overview of $OCuGa_3$ polyhedra in 3R $CuGaO_2$ structure.