Packing of Russian Doll Clusters to Form a Nanometer-Scale CsCl-type Compound in a Cr-Zn-Sn Complex Metallic Alloy

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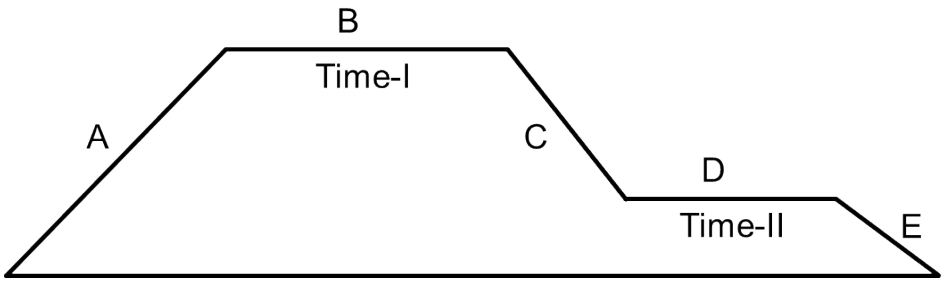
SUPPORTING INFORMATION

Summary of synthetic procedures: The schematic figure and table summarize the experimental procedures to prepare $Cr_{22}Zn_{72}Sn_{24}$ carried out during this investigation. The loading compositions for the procedures I, III, IV, V, and VI are Cr: Zn: Sn= 1:6:2 (by moles). The loading composition for procedure II is Cr: Zn: Sn= 1:3:3. (Procedures I and II yielded crystals and procedure II has the highest crystal yield.)



Procedure	A (°C/min)	B (°C)	C (°C/min)	D (°C)	E	Time-I (hr)	Time-II (hr)
I	1	850	0.02	200	Quench	24	72
II	1	850	1	600	Spin	24	72
III	1	850	1	200	Quench	24	72
IV	1	850	1	500	Quench	24	72
V	1	850	1	600	Quench	24	72
VI	1	850	1	700	Quench	24	72

Table S1. Powder X-ray diffraction refined parameters of using Rietveld analysis of $Cr_{22}Zn_{72}Sn_{24}$ at 293K.

Crystallographic unit cell: cubic (space group: *Fm-3c*), $a = b = c = 25.2562(1)$ Å, $Rp = 4.588$, $Rwp = 5.084$.

Atom	*Wyckoff*	*Occupancy*	*x*	*y*	*z*	*U*(*eq*) (Å)
Cr1	8*a*	1	¼	¼	¼	0.042
Cr2	8*b*	1	0	0	0	0.045
Cr3	64*g*	1	0.19441	0.19441	0.19441	0.054
Cr4	96*i*	1	0	0.10998	0.16782	0.045
Zn5	192*j*	¼	0.13832	0.27097	0.26737	0.051
Zn6	48*e*	1	0.18984	0	0	0.054
Zn7	96*i*	1	0	0.05511	0.08944	0.046
Zn8	96*i*	1	0	0.21475	0.14173	0.045
Zn9	96*h*	1	¼	0.05701	0.05701	0.045
Zn10	192*j*	1	0.05372	0.14996	0.09111	0.048
Sn11	192*j*	1	0.08802	0.16267	0.20472	0.050

Table S2. Selected crystallographic data at 293(2) K for additional crystalline specimens extracted from the Cr-Zn-Sn product.

Specimen	**A**	**B**	**C**
Refined Formula	$Cr_{22}Zn_{72}Sn_{24}$	$Cr_{22}Zn_{72}Sn_{24}$	$Cr_{22}Zn_{72}Sn_{24}$
Crystal Size	Irregular shape with radius of ca. 0.015mm		
F.W. (g/mol); F(000)	4349.60; 31104	4349.60; 31104	4349.60; 31104
Space group; *Z*	$Fm\bar{3}c$ (No. 226); 16	$Fm\bar{3}c$ (No. 226); 16	$Fm\bar{3}c$ (No. 226); 16
Lattice Parameter *a* (Å)	25.225(5)	25.179(7)	25.163(10)
Volume (Å^3)	16051(5)	15962(8)	15933(11)
d_{calc} (mg/m^3)	7.200	7.240	7.253
Absorption Correction	Multi-scan	Multi-scan	Multi-scan
μ(mm^{-1})	31.166	31.340	31.397
θ range (°)	1.61 to 28.40	1.62 to 28.30	1.63 to 28.31
hkl ranges	$-33 \le h,k,l \le 33$	$-32 \le h,k,l \le 32$	$-33 \le h,k,l \le 33$
No. of reflections [I > 2σ(I)]	31824	30763	31563
No. independent reflections; R_{int}	911; 0.0613	891; 0.1055	896; 0.1463
No. parameters	60	60	60
R_1; wR_2 [I > 2σ(I)]	0.0312; 0.0702	0.0342; 0.0613	0.0412;0.0808
R_1; wR_2 (all *I*)	0.0355; 0.0760	0.0398; 0.0616	0.0614; 0.0845
Goodness of fit	1.072	1.110	1.078
Diffraction peak and hole (e$^-$/Å^3)	4.166; –2.927	2.665; –2.775	2.239; –2.420

Table S3. Anisotropic temperature factors for $Cr_{22}Zn_{72}Sn_{24}$ at 293(2) K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr1	0.005(1)	0.005(1)	0.005(1)	0	0	0
Cr2	0.007(1)	0.008(1)	0.006(1)	–0.000(1)	0	0
Zn3	0.011(1)	0.015(1)	0.009(1)	0	0	0
Zn4	0.010(1)	0.010(1)	0.008(1)	–0.001(1)	0	0
Zn5	0.017(1)	0.013(1)	0.019(1)	0.001(1)	0	0
Zn6	0.009(1)	0.014(1)	0.014(1)	0.002(1)	0.001(1)	–0.001(1)
Zn7	0.015(1)	0.011(1)	0.010(1)	0.002(1)	0.002(1)	0.001(1)
Sn8	0.015(1)	0.020(1)	0.018(1)	0.001(1)	–0.004(1)	–0.006(1)
Cr9	0.005(1)	0.005(1)	0.005(1)	0	0	0
Cr10	0.047(1)	0.047(1)	0.047(1)	–0.018(1)	–0.018(1)	–0.018(1)
Zn11	0.047(3)	0.077(7)	0.012(7)	0.076(6)	0.095(7)	0.050(4)

Table S4. Structural features of three cubic CMAs related to $Cr_{22}Zn_{72}Sn_{24}$. *R* designates the distance of the atomic shell from the corresponding center of either the 8*b* (center of *I*13-cluster) or the 8*a* (bcc cluster) sites.

CMA:	$Cr_{11}Zn_{36}Sn_{12}$ (216 e^-)		$Mo_7Zn_{38.7}Sn_{12}$[7] (224.4 e^-)		$Ru_{13}Zn_{33.5}Sb_{12}$[32] ("**CA**"; 278.0 e^-)		$V_7Zn_{39}Ga_{12}$[31] (209 e^-)	
Pearson Symbol	*cF*944		*cF*922.88		*cF*936.64		*cF*928	
a (Å)	25.184		25.447		25.098		24.857	
Wyckoff Site in $Fm\bar{3}c$	Atom	*R* (Å)	Atom	*R* (Å)	Atom	*R* (Å)	Atom	*R* (Å)
				---*I*13-Cluster---				
8*b*	Cr	---	Mo	---	Ru	---	V	---
96*i*	Zn	2.586	Zn	2.626	Zn	2.555	Zn	2.646
48*e*	Zn	4.478	Zn	4.519	Zn	4.524	Zn	4.469
192*j*	Zn	4.560	Zn	4.611	Zn	4.653	Zn	4.679
96*i*	Cr	5.222	Mo	5.292	Ru	4.989	V	5.215
96*h*	Zn	6.608	Zn	6.674	Zn	6.610	Zn	6.567
96*i*	Zn	6.659	Zn	6.714	Ru	7.973	Zn	6.763
192*j*	Sn	7.032	Sn	7.065	Sb	6.921	Ga	6.913
				bcc Cluster				
8*a*	Cr	---	Mo	---	Ru	---	V	---
64*g*	Cr	2.600	0.91 Zn	2.649	0.24 Zn	2.627		
192*j* / 48*f*	Zn	2.513	0.68 Zn	2.804	0.34 Zn	2.549		
96*h*							Zn	2.724
24*d*					Zn	6.275		

Figure S1. TEM diffraction patterns of the crystalline [001] axes for $Cr_{22}Zn_{72}Sn_{24}$.

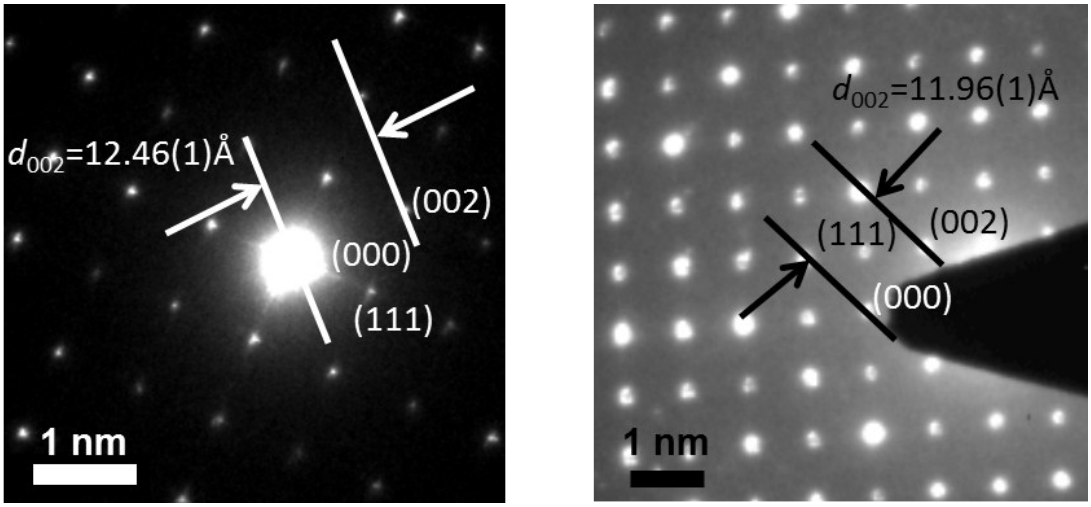


Figure S2. Electronic density distribution in $Cr_{22}Zn_{72}Sn_{24}$ without the Zn11 (192*j*) site along the *x*-axis.

***x*=0.158**