$EuAg_xAl_{11-x}$ with the $BaCd_{11}$-Type Structure: Phase Width, Coloring, and Electronic Structure

Fei Wang,[†] *Karen Nordell Pearson,*[‡] *and Gordon J. Miller**[,†]

[†] Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

[‡] Department of Chemistry, Lawrence University, Appleton, Wisconsin 54912, USA

Supplementary Material

Powder X-ray Diffraction Patterns of $EuAg_xAl_{11-x}$.

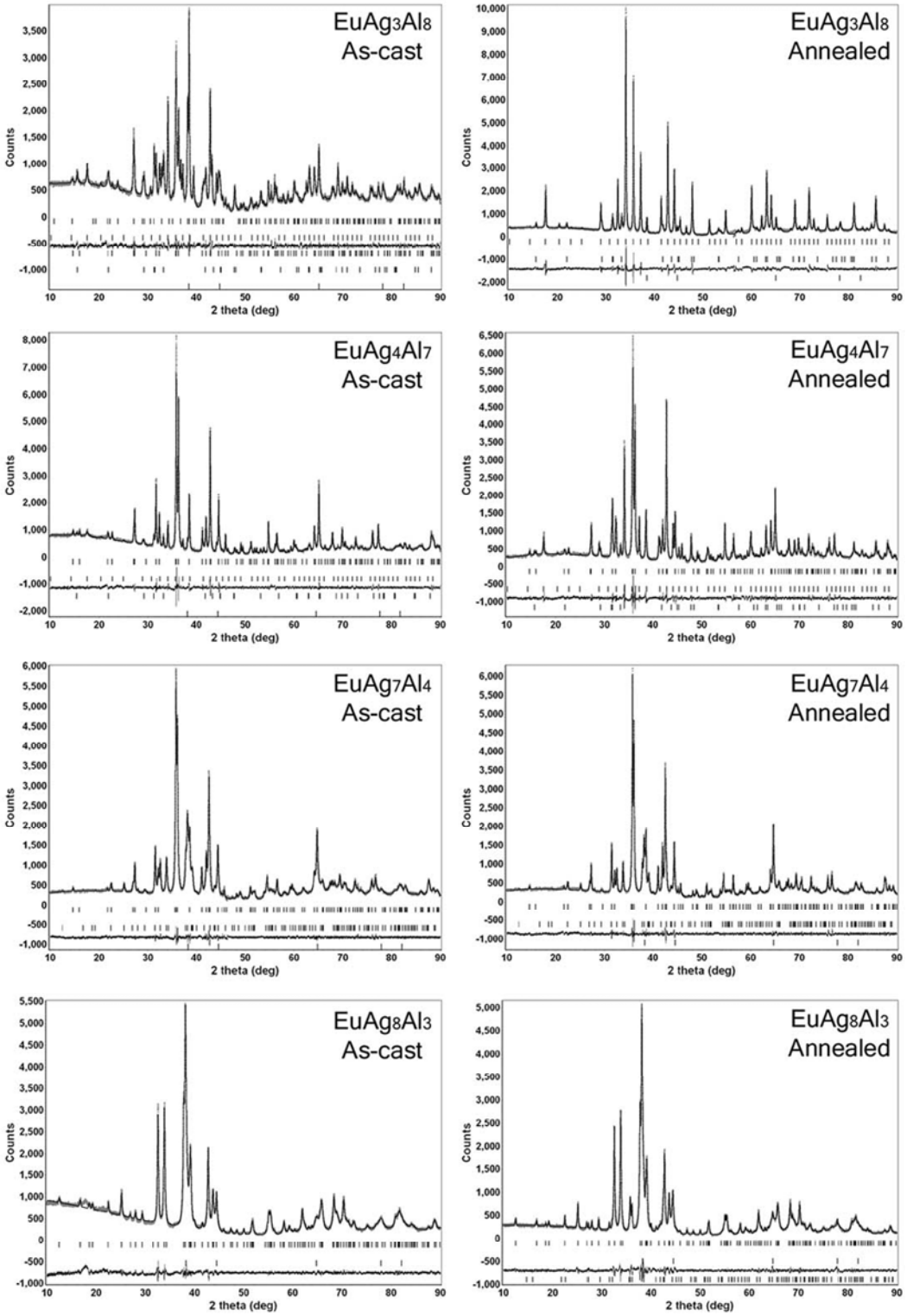

Figure S1. The powder XRD patterns of $EuAg_xAl_{11-x}$ samples (x = 3, 4, 7, 8).

The X-ray diffraction patterns for the $EuAg_xAl_{11-x}$ series ($3 \leq x \leq 8$) are shown in Figure S1. For $EuAg_3Al_8$, annealing has a significant effect. The as-cast sample is a mixture of 5 phases: $BaHg_{11}$-type, $BaCd_{11}$-type, Th_2Ni_{17}-type, $BaAl_4$-type, and *fcc* (an Ag-Al binary alloy). After annealing, only the $BaHg_{11}$-type and $BaAl_4$-type phases can be detected by powder XRD and the former became the dominating phase. Further study is focusing on this $BaHg_{11}$-type structure and the results will be included in a subsequent report. The as-cast $EuAg_4Al_7$ sample consists of $BaHg_{11}$-type, $BaCd_{11}$-type, $BaAl_4$-type, and *fcc* phases. Annealing increased the abundance of the $BaHg_{11}$-type phase. The $EuAg_7Al_4$ sample is composed with $BaCd_{11}$-type, Th_2Zn_{17}-type, and *fcc* phases. Annealing did not perceptibly change the phases. The as-cast $EuAg_8Al_3$ sample gives an almost pure Th_2Zn_{17}-type phase. The $BaCd_{11}$-type phase shows its diffraction peaks after annealing.

The Crystallographic Data of $EuAg_6Al_5$ samples

Table S1. The crystallographic data and selected refinement parameters of the crystals selected from $EuAg_6Al_5$ samples (both as-cast and annealed).

	As-cast	Annealed
Empirical formula	$EuAg_{5.80(7)}Al_{5.20(7)}$	$EuAg_{6.02(5)}Al_{4.98(5)}$
Space group	$I4_1/amd$ (No. 141)	$I4_1/amd$ (No. 141)
Lattice parameters	a = 11.0907(11) Å	a = 11.102(3) Å
	c = 7.1174(10) Å	c = 7.125(2) Å
Volume	875.47(17) Å^3	878.3(4) Å^3
θ range	3.40°-28.30°	3.40°-28.26°
Z	4	4
	$-14 \le h \le 14$	$-14 \le h \le 14$
Index ranges	$-14 \le k \le 14$	$-11 \le k \le 14$
	$-9 \le k \le 9$	$-9 \le k \le 9$
Reflections collected	3556	3567
Independent reflections	306 (R_{int} = 0.0469)	306 (R_{int} = 0.0814)
Data/restraints/parameters	306/0/21	306/0/21
Goodness-of-fit on F^2	1.237	1.058
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0275; wR2 = 0.0493	R1 = 0.0295; wR2 = 0.0490
R indices (all data)	R1 = 0.0305; wR2 = 0.0499	R1 = 0.0423; wR2 = 0.0529
Largest diff. peak/hole	1.167/–2.012 e$^-$/ Å^3	1.710/–1.186 e$^-$/ Å^3

Maximizing the Number of Ag-Al Contacts in $EuAg_6Al_5$.

The coloring scheme with the maximal number of Ag-Al contacts was found by generating all possible schemes and counting their connections, which was performed by a short program written in the C language. The algorithm is as follows:

Instead of the body-centered complete unit cell (Z = 4; 44 Ag/Al atoms), the primitive cell (Z = 2; 22 Ag/Al atoms) was used for scheme generating and Ag-Al contacts counting to reduce the computation time. The primitive cell vectors are: (***a***, ***b***, and ***c*** are the basic vectors of the complete unit cell)

$$\boldsymbol{a}' = -0.5\boldsymbol{a} + 0.5\boldsymbol{b} + 0.5\boldsymbol{c};$$

$$\boldsymbol{b}' = \ \ 0.5\boldsymbol{a} - 0.5\boldsymbol{b} + 0.5\boldsymbol{c};$$

$$\boldsymbol{c}' = \ \ 0.5\boldsymbol{a} + 0.5\boldsymbol{b} - 0.5\boldsymbol{c}.$$

The 22 sites for Ag and Al in the primitive cell are listed in Table S2. By reducing the symmetry to triclinic (space group *P1*), the 22 sites are all symmetrically independent.

For the composition of $EuAg_6Al_5$, 12 out of the 22 sites should be assigned to Ag and the other 10 to Al. The total number of possible coloring schemes is:

$$\frac{22!}{12!\times 10!} = 646,646 .$$

All of these coloring schemes were generated and their Ag-Al contacts were counted. To count them, each of the 22 atoms in the primitive cell was tested against all the atoms in the same cell as well as the 26 neighboring cells (6 face-sharing, 12 edge-sharing, and 8 vertex-sharing). A Ag-Al contact was counted as 1 if it was within the same cell, and as 0.5 if it was between two neighboring cells. Through this the number of Ag-Al connections per primitive cell was obtained.

The maximal number of Ag-Al contacts was found in 4 coloring schemes (Models **5**-**8**, Table S2). They give the same coordination environment of Eu atoms (Figure 4e and 4f) and are thus structurally equivalent. So only one of them (Model **5**) was taken for the first principal calculation.

Table S2. The 22 Ag/Al sites in the primitive cell and the 4 equivalent coloring schemes found by maximizing the number of Ag-Al contacts in $EuAg_6Al_5$.

Wyck. in Complete Cell	Fractional Coordinates in Complete Cell			Model **5**	Model **6**	Model **7**	Model **8**
	x	*y*	*z*				
4b	1/2	−1/4	−1/8	Ag	Ag	Ag	Ag
	−1/2	1/4	1/8	Ag	Ag	Ag	Ag
8d	0	0	1/2	Al	Al	Ag	Ag
	1/4	1/4	1/4	Ag	Al	Ag	Al
	−1/4	1/4	1/4	Al	Ag	Al	Ag
	1/2	0	0	Ag	Ag	Al	Al
32i	0.1198	0.0442	0.1740	Al	Ag	Al	Ag
	0.1198	–0.0442	–0.1740	Ag	Al	Ag	Al
	–0.1198	0.0442	0.1740	Ag	Al	Ag	Al
	–0.1198	–0.0442	–0.1740	Al	Ag	Al	Ag
	0.2942	0.1302	–0.0760	Al	Al	Ag	Ag
	0.2942	–0.1302	0.0760	Al	Al	Ag	Ag
	–0.2942	0.1302	–0.0760	Al	Al	Ag	Ag
	–0.2942	–0.1302	0.0760	Al	Al	Ag	Ag
	0.2058	0.1302	–0.4240	Ag	Ag	Al	Al
	–0.2058	–0.1302	0.4240	Ag	Ag	Al	Al
	0.3802	–0.0442	–0.3260	Ag	Al	Ag	Al
	–0.3802	0.0442	0.3260	Ag	Al	Ag	Al
	0.2942	–0.3698	0.0760	Ag	Ag	Al	Al
	–0.2942	0.3698	–0.0760	Ag	Ag	Al	Al
	–0.1198	0.5442	–0.1740	Al	Ag	Al	Ag
	0.1198	–0.5442	0.1740	Al	Ag	Al	Ag