Exploring New Zintl Phases in the 9-4-9 family via Al Substitution. Synthesis, Structure and Physical Properties of $Ae_9Mn_{4-x}Al_xSb_9$ (Ae = Ca, Yb, Eu)

Xiao-Cun Liu,[*,†] Ke-Feng Liu,[‡] Qi-Qi Wang,[‡] Yan-Min Wang,[†] Ming-Yan Pan,[§] Sheng-Qing Xia[*‡]

† *School of Civil Engineering, Shandong Jiaotong University, Jinan, Shandong 250023, P. R. China*

‡ *State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan, Shandong 250100, P. R. China*

§ *Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, Shanghai 201800, China*

Supporting Information

Contents

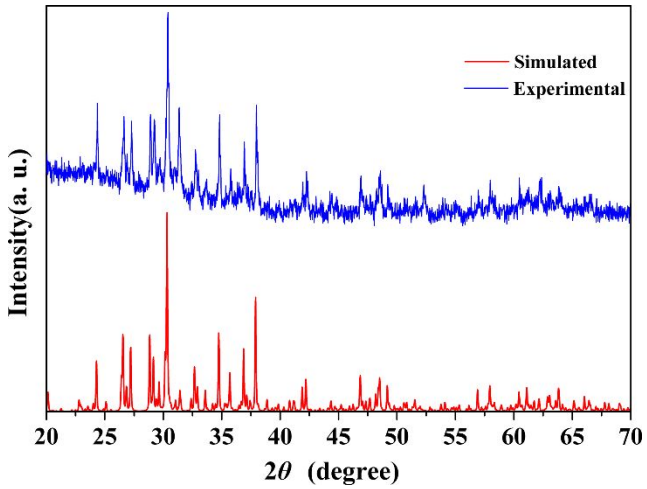
1. Table S1. Atomic positions and anisotropic displacement parameters of $Yb_9Mn_{3.59(6)}Al_{0.41}Sb_9$.

Atoms	Wyckoff site	*x*	*y*	*z*	site occupancy	U_{eq} (Å^2)
Ca1	*2a*	0	0	0	1	0.01589(17)
Ca2	*4h*	0.11795(4)	0.23708(2)	1/2	1	0.01252(13)
Ca3	*4h*	0.05615(4)	0.40823(2)	1/2	1	0.01186(13)
Ca4	*4h*	0.28023(4)	0.10191(2)	0	1	0.01540(13)
Ca5	*4g*	0.36096(4)	0.36235(2)	1/2	1	0.01431(13)
Mn1/Al1	*4g*	0.21855(14)	0.45464(8)	0	0.915(15)/0.085	0.0105(6)
Mn2/Al2	*4g*	0.21855(14)	0.45464(8)	0	0.881(16)/0.119	0.0105(6)
Sb1	*2c*	0.37917(15)	0.25780(8)	0	1	0.0121(6)
Sb2	*4g*	0.37917(15)	0.25780(8)	0	1	0.0121(6)
Sb3	*4g*	0	0.5	0	1	0.0106(2)
Sb4	*4h*	0.03380(6)	0.14823(3)	0	1	0.00952(16)
Sb5	*4h*	0.18527(6)	0.33152(3)	0	1	0.00864(16)

2. Table S2. Important interatomic distances (Å) in $Ca_9Mn_{2.91(4)}Al_{1.09}Sb_9$ and $Eu_9Mn_{2.87(4)}Al_{1.13}Sb_9$.

$Ca_9Mn_{2.91(4)}Al_{1.09}Sb_9$					$Eu_9Mn_{2.87(4)}Al_{1.13}Sb_9$				
Mn1	—	Sb3		2.7580(11)	Mn1	—	Sb2	×2	2.7215(8)
	—	Sb4	×2	2.7631(6)	Mn1	—	Sb6	×2	2.8245(10)
	—	Sb1		2.8475(11)	Mn2	—	Sb7	×2	2.7970(9)
Mn2	—	Sb5	×2	2.7374(7)	Mn2	—	Sb4		2.9399(17)
	—	Sb2		2.7873 (12)	Mn2	—	Sb1		2.9736(16)
	—	Sb3		2.8725(12)	Mn3	—	Sb7	×2	2.7728(9)
					Mn3	—	Sb3		2.7779(16)
					Mn3	—	Sb3		2.9423(16)
					Mn4	—	Sb4		2.659(2)
					Mn4	—	Sb6	×2	2.7102(11)
					Mn4	—	Sb5		2.797(2)

3. Figure S1. Powder XRD patterns of $Eu_9Mn_{2.87(4)}Al_{1.13}Sb_9$ recorded at room temperature. The theoretical calculated patterns are provided for comparison as well.



4. Figure S2. Coordination geometry plot for various Eu cations in $Eu_9Mn_{2.87(4)}Al_{1.13}Sb_9$.