



(Ca/Sr)Au_xCd_{1-x}: Stacking variants of the CrB–FeB series

Wiebke Harms, Ines Dürr, Michael Daub, Caroline Röhr*

Institut für Anorganische und Analytische Chemie, University of Freiburg, Albertstr. 21, D-79104 Freiburg, Germany

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ABSTRACT

The structural chemistry of binary 1:1 alkaline earth metallides $A^II M$ ($M = p$ -block or late transition element) is dominated by planar M zig-zag chains, which are stacked in different orientations (CrB (c) to FeB (h) type) and with variable stacking distances (types I and II). As a case study of the electronic influences, the substitution of Au against Cd in the respective Ca and Sr aurides was examined by means of experimental, crystallographic and computational methods. Starting from CaAu, up to 11% of Au can be substituted by Cd without a change in the CrB structure type (orthorhombic, space group $Cmcm$, $a = 398.2(1)$, $b = 1122.6(6)$, $c = 460.9(2)$ pm, $Z = 4$, $R1 = 0.0303$). Starting from SrAu (stacking sequence $(hc)_2(h_2c)_2$), depending on the proportion of the Cd substitution a successive change to structures with increased hexagonality is observed: In SrAu_{0.93}Cd_{0.07} (monoclinic, space group $P2_1/m$, $a = 621.3(4)$, $b = 472.4(2)$, $c = 1216.1(9)$ pm, $\beta = 96.97(5)^\circ$, $Z = 6$, $R1 = 0.0467$) the stacking sequence is h_2c , i.e. the hexagonality is 66.67%. A slightly more increased Cd content in SrAu_{0.78}Cd_{0.22} (orthorhombic, space group $Pnma$, $a = 3243.3(8)$, $b = 474.17(8)$, $c = 626.20(9)$ pm, $Z = 16$, $R1 = 0.0682$) drives the hexagonality to 75%, with a $(h_3c)_2$ stacking sequence known from several rare earth nickel compounds. Further Cd substitution is not possible. However, in the Cd-rich section of the two series, where the CsCl/ β -brass structure type occurs for both alkaline earth elements, a small Au substitution, as determined from powder data by Rietveld refinements, is possible. The substitution limit and the stability ranges of the CsCl and the CrB type can be rationalized from the calculated band structures. Geometrical and electronic criteria are used to compare and discuss the stability ranges in a structural map.

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1. Introduction

The structural chemistry of binary 1:1 alkaline earth metallides $A^II M$ ($M = p$ -block or late transition element) is dominated by planar M zig-zag chains, which are stacked in different orientations (CrB- to FeB-type) and with variable stacking distances (type I and II). The change from the CrB-I type (stretched trigonal A prisms around M) to the respective type II structures (compressed prisms), driven by the valence electron concentration (v.e.c.), is already discussed in the literature [1,2] and has recently been examined in more detail for the phase width AM^{14} (v.e./ $M = 6$)– AM^{13} (v.e./ $M = 5$) by means of crystallographic and computational studies [3]. CaGa is the only compound of this structure family with v.e./ $M = 5$, while the binary monoindides [4] and mixed trielides [5] form other singular structures. For the compounds $A^II Zn$ with v.e./ $M = 4$, the structures change from the CrB-II type (CaZn [6]) to the FeB-II type (SrZn [1]) or the simple CsCl type of BaZn [7] is obviously driven by the decreasing radius ratio r_M/r_A . On the other hand, in the silver series (CaAg: CrB-II [1]–SrAg: dimorphic with two complicated stacking variants [8]–BaAg: FeB-II [8]), i.e. at v.e./ $M = 3$, five different stacking variants

have been observed [9]. In this case, the successive change from pure cubic (CrB-II) to exclusively hexagonal stacking (FeB-II) is also obviously caused by the change of the radius ratio. Similar size-dependent CrB–FeB stacking series have been observed for the $LnNi$ binary and ternary intermetallics (v.e./ $M = 3.0$) [10–12]. For a case study of the electronic influences, the substitution of Au against Cd in the respective Ca and Sr aurides was chosen over the argentides as a differentiation of Ag and Cd via X-ray diffraction methods is not possible. Argentides and aurides (CaAu: CrB-II [1]–SrAu: singular structure type with 60% hexagonality [8]) show a comparable radii dependent stacking sequence change (although possible stacking variants inbetween are not yet confirmed for the aurides) and a broad variety of stacking variants is already known for the series CaCu–CaM ($M = Ga$ [13], Zn [14], Ge [13], etc.), CaAg–CaZn [15], SrAg–SrZn [13] and SrCu–SrCd [16].

2. Experimental section

2.1. Preparation

The synthesis of the title compounds was generally performed starting from the elements calcium or strontium, cadmium and gold obtained from commercial sources and used without further purification (Ca: Aldrich, 99%; Sr: Metallhandelsgesellschaft

* Corresponding author.

E-mail address: caroline@ruby.chemie.uni-freiburg.de (C. Röhr).

Maassen, Bonn, 99%; Au: Heraeus GmbH, 99.99% and Cd: ABCR Karlsruhe, 99.999%). The educts were filled into tantalum crucibles under an argon atmosphere. The sealed containers were heated in corundum tubes under a static Ar atmosphere to a maximum temperature of 1375 K with constant heating/cooling rates given in Table 1 for all samples. Representative parts of the reguli were ground and sealed in capillaries with a diameter of 0.3 mm. X-ray powder diagrams were collected on a transmission powder diffractometer system (STADI P, linear PSD, Fa. Stoe & Cie, Darmstadt, MoK α radiation, graphite monochromator).

For the Ca series, four samples were prepared along the section CaAu $_x$ Cd $_{1-x}$. In all cases the powder patterns of the samples showed the formation of 1:1 compounds exclusively: For Au contents x between 0.1 and 0.3, the CsCl type structures are formed in pure phase, however with very low crystal qualities. For that reason, a Rietveld refinement of the X-ray powder pattern was preferred to a single crystal structure determination. In all

cases the Au/Cd proportion of the statistically occupied positions fits the sample composition. At a 1:1 proportion of Au:Cd, the sample contains both the most Au-rich compound with the CsCl structure type, CaAu $_{0.29}$ Cd $_{0.71}$, and the most Cd-rich phase with the CrB structure type, CaAu $_{0.89}$ Cd $_{0.11}$. This product composition thus nicely demonstrates the phase width of the CsCl (Cd-rich) and the CrB type (Au-rich) structure. Also, the fact that in samples with a Au content of 80% small amounts of the CsCl type can be identified from the powder diffraction diagram confirms the mentioned composition ranges of the two structure types.

In the case of the respective strontium series, the powder pattern of the Au-rich sample of composition SrAu $_{0.8}$ Cd $_{0.2}$ can be fully indexed using the theoretical diffraction diagram of the monoclinic phase SrAu $_{0.93}$ Cd $_{0.07}$ (crystal data see Tables 3 and 4). Evidently, in this case a small loss of cadmium occurs, which can be easily explained from the high volatility of Cd. In the Cd-rich samples with

Table 1
Details of the synthesis of the Ca/Sr–Au–Cd compounds.

Sample composition	Weighted sample						T program			Phase composition from powder data (structure type)
	A		Au		Cd		$\dot{T} \uparrow$ (K/h)	T_{\max} (K)	$\dot{T} \downarrow$ (K/h)	
	mg	mmol	mg	mmol	mg	mmol				
CaAu $_{0.8}$ Cd $_{0.2}$	182.6	4.56	714.8	3.63	102.2	0.91	30	1375	20	CaAu $_{0.9}$ Cd $_{0.1}$ (CrB)
CaAu $_{0.5}$ Cd $_{0.5}$	206.3	5.15	505.4	2.57	289.2	2.57	30	1375	20	CaAu $_{0.89}$ Cd $_{0.11}$ (CrB); CaAu $_{0.29}$ Cd $_{0.71}$ (CsCl)
CaAu $_{0.3}$ Cd $_{0.7}$	225.2	5.62	333.1	1.69	442.8	3.94	200	1375	20	CaAu $_{0.29}$ Cd $_{0.71}$ (CsCl)
CaAu $_{0.1}$ Cd $_{0.9}$	249.6	6.23	123.0	0.62	628.9	5.59	200	1375	20	CaAu $_{0.13}$ Cd $_{0.87}$ (CsCl)
SrAu $_{0.8}$ Cd $_{0.2}$	328.1	3.74	588.0	2.96	84.1	0.75	200	1375	20	SrAu $_{0.93}$ Cd $_{0.07}$ (Y $_{0.3}$ Gd $_{0.7}$ Ni)
SrAu $_{0.5}$ Cd $_{0.5}$	362.2	4.13	405.8	2.04	231.3	2.06	200	1375	20	SrAu $_{0.92}$ Cd $_{0.08}$ (Y $_{0.3}$ Gd $_{0.7}$ Ni), SrCd $_2$
SrAu $_{0.2}$ Cd $_{1.8}$	399.1	4.55	179.4	0.90	921.6	8.20	200	1375	10	SrAu $_{0.78}$ Cd $_{0.22}$ (CaCu $_{0.8}$ Zn $_{0.2}$), SrCd $_2$

Table 2
Crystallographic data, details of the data collection and structural determination for the compounds CaAu $_{0.89}$ Cd $_{0.11}$, CaAu $_{0.29}$ Cd $_{0.71}$ and CaAu $_{0.13}$ Cd $_{0.87}$.

Compound	CaAu $_{0.89}$ Cd $_{0.11}$	CaAu $_x$ Cd $_{1-x}$	CaAu $_{0.13}$ Cd $_{0.87}$
x	0.89	0.29(2)	0.13(1)
Structure type	CrB-II		CsCl
Stacking sequence	c		–
Hexagonality (%)	0		–
Crystal system	Orthorhombic		Cubic
Space group	$Cmcm$, no. 63		$Pm\bar{3}m$, no. 221
Lattice constants (pm)			
a	397.7(2)	378.15(7)	382.29(4)
b	1122.7(6)	–	–
c	461.5(1)	–	–
Volume of the u.c. (10 6 pm 3)	206.0	54.07(3)	55.87(2)
Z	4		1
Density (X-ray) (g/cm 3)	7.29	5.43	4.86
Diffractometer	Stoe IPDS-2		Stoe STADI-P
Absorption coeff. $\mu_{\text{MoK}\alpha}$ (mm $^{-1}$)	MoK α radiation, graphite monochromator		
θ range (deg)	65.61	–	–
No. of reflections collected	3.6–27.8		4.0–40.0
No. of independent reflections	1303	–	–
R_{int}	156	–	28
Corrections	0.0854	–	–
Refinement	Lorentz, polarization, absorption		
No. of free parameters	SHELXL-97 [18]		GSAS [20]
Goodness-of-fit on F^2	10		22
R values (for refl. with $I \geq 2\sigma(I)$)	1.119		–
R_1	0.0308	$R_1 = 0.0778$	$R_1 = 0.0268$
wR_2	0.0733	$R_p = 0.0578$	$R_p = 0.0499$
R values (all data)			
R_1	0.0308	–	–
wR_2	0.0733	–	–
Residual elect. density (e $^-$ 10 $^{-6}$ pm $^{-3}$)	2.0/–1.8	–	–

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