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Alteration of rare-earth-metal cluster iodides $R(R_6I_{12}Z)$ through cation substitution

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Abstract

Four examples of $(A_xR_{1-x})R_6I_{12}Z$ phases further illustrate the flexibility of the rhombohedral $R_7X_{12}Z$ structure to substitution of heterocations for the isolated R^{III} atoms without destruction of the structure. The examples with $R = \text{La, Pr, Z} = \text{Fe, Co, Ir}$, and stoichiometric amounts of $A = \text{Na or Ca}$ were prepared by traditional high temperature techniques and characterized by single crystal and Guinier powder X-ray diffraction techniques. Product compositions refined in the parent space group $R\bar{3}$ from reactions of stoichiometry $AR_6I_{12}Z$ were $(\text{Na}_{0.90}\text{Pr}_{0.10})\text{Pr}_6\text{I}_{12}\text{Ir}$, $(\text{Na}_{0.954}\text{La}_{0.046})\text{La}_6\text{I}_{12}\text{Fe}$, and $(\text{Ca}_{0.801}\text{La}_{0.199})\text{La}_6\text{I}_{12}\text{Co}$. More general characteristics of and trends in the family of $R_7X_{12}Z$ structures are also considered, including distortions of the ideal motif as a function of extremes in the components.

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1. Introduction

The rhombohedral $R_7X_{12}Z$ structure type is known for its wide variety of possible rare-earth metals R , halogens X (Cl, Br, I), and transition metal interstitials Z that may be employed. It is one of only three structure types for the rare-earth metals that exhibit isolated R_6X_{12} clusters (the others being $R_{12}X_{17}Z$ and $R_6X_{10}Z$), although many additional compounds are known that are built of infinite chains or networks of condensed clusters. The vast array of compositions among all rare-earth-metal cluster halides arises in part because of both the large variety of possibilities for both possible intercluster bridging modes for halide and a sizeable range of workable Z [1,2].

The rhombohedral $R_7X_{12}Z$ structure, Fig. 1, consists of R_6 trigonal antiprismatic clusters with $\bar{3}$ symmetry which are dimensionally only slightly distorted from ideal octahedra [3–5]. The Z (small black) atoms that evidently must be bound in the center of every cluster may consist of most of the group 7–11 transition metals as well as a variety of light main-group elements [2,6].

As usual, all 12 R – R edges of the metal cluster are bridged by one of two crystallographically distinct X atoms (white). Six $X1$ -type halides bridge the R – R edges of the top and bottom triangular (basal) faces (as X^i). The other six edges about the waist of the cluster are bridged by $X2$ atoms that also form exo bonds to metal vertices of adjacent clusters (X^{i-a}). Reciprocally, the metal atom vertices of each cluster are terminally bonded to $X2$ atoms that bridge R – R waist edges of neighboring clusters (X^{a-i}). Finally, the seventh R atom (the larger gray sphere, crystallographically $R2$) and the substitution site is located halfway between R_6Z clusters at $0, 0, \frac{1}{2}$ and is trigonal antiprismatically surrounded by six $X1$ atoms, three from the cluster below and three from the cluster above. Accordingly, a more description formulation for $R_7X_{12}Z$ is $R2^{3+}[(R1)_6(Z)(X1^i)_6(X2^{i-a})_{6/2}(X2^{a-i})_{6/2}]^{3-}$.

Introduction of alkali or alkaline-earth-metal cations into rare-earth-metal cluster halide structures generally produces either new arrays with more reduced clusters or, when accompanied by halide, more open structural frameworks that accommodate the added cations. Functionally, the cations mainly fulfill charge requirements, as in $AR_6I_{10}Z$ ($A = \text{K, Cs}$; $R = \text{La, Pr}$; $Z = \text{Mn, Fe, Os}$) [7], $\text{Cs}_4\text{R}_6\text{I}_{13}\text{Z}$, $R = \text{Ce, Pr}$; $Z = \text{Co, Os}$) [8], and

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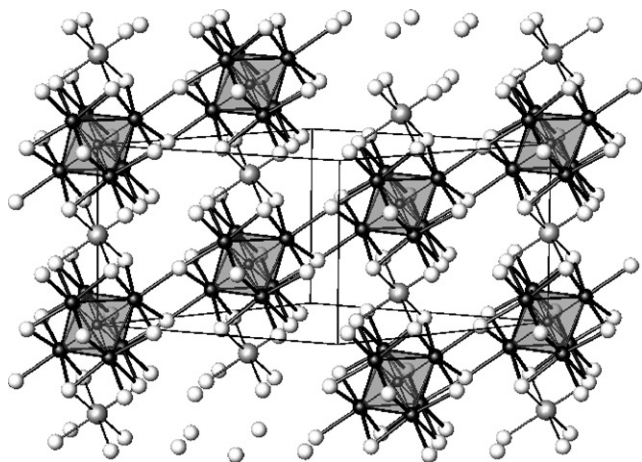


Fig. 1. \sim [110] view of the rhombohedral structure of $\text{Na}_{0.90}\text{Pr}_{0.10}$ ($\text{Pr}_6\text{I}_{12}\text{Ir}$). Black atoms in shaded clusters are smaller—Ir, larger—Pr; open spheres are I; larger gray spheres are Na(Pr) (c lies vertical). In the parent $\text{Pr}_7\text{I}_{12}\text{Ir}$, the Na position is occupied only by Pr.

in $\text{Cs}_2\text{La}_{10}\text{I}_{17}\text{Co}_2$ with biotetrahedral clusters [9]. Recently, a series of isostructural compounds ($A_x\text{La}_{1-x}\text{La}_6\text{I}_{12}\text{Os}$ ($A = \text{Li, Na, Mg, Ca, Sr}$)) has been discovered that greatly enlarged the range of phases possible with the nominal $R_7X_{12}Z$ structure type [10–12]. Cations of the listed A elements in fact appear to substitute for the isolated R cations over a continuous range ($0 < x \leq 1.0$) without destruction of the structure. The magnitude of the substitution in these cases depends on the loaded proportions of the AI or AI_2 reactants and, of course, the relative stabilities of alternate products. Substantially complete substitution is possible at least for Li, Na, Ca, Sr with stoichiometric or only moderate excesses of added cation iodide according to single crystal refinements. Analogous results were also obtained with some neighboring platinum metal interstitials in place of Os.

One of the reasons for undertaking the present investigation were the results of earlier, brief attempts to achieve like replacements of R_2 in other $R_7I_{12}Z$ phases by Ca [4]. In these cases, only partial substitution was achieved in a twinned example of $(\text{Ca}_{0.65}\text{Pr}_{0.35})\text{Pr}_6\text{I}_{12}\text{Co}$ whereas $(\text{Ca}_y\text{Gd}_{1-y})\text{Gd}_6\text{I}_{12}\text{Fe}$ and $(\text{Ca}_z\text{Gd}_{1-z})\text{Gd}_6\text{I}_{12}\text{Co}$ appeared to exhibit less substitution according to powder diffraction data. The present study sought to establish whether the utilization of $3d$ interstitials or of later rare-earth cluster elements might have been responsible for these twinning and limited reaction processes. These and earlier results are also given a more general consideration of cluster stabilities and structures.

2. Experimental

The general techniques, including the use of welded Ta containers and Guinier powder diffraction, have

been described before [10,11,13]. All manipulations were carried out within N_2 - or He-filled gloveboxes.

2.1. Synthesis

Elemental Na (Fisher, 99.9%), Co (Alfa Aesar, 99.5%), Ir and Fe (Alfa Aesar, 99.9%) were stored in an N_2 -filled glovebox and used as received. The binary iodides NaI (Mallinckrodt, 99.9%) and CaI_2 (Alfa Aesar, 99.5%) were dried and sublimed under dynamic vacuum before storage in the glovebox. Iodine (Fisher, 99.8%) was used as received. The rare-earth-metal triiodides LaI_3 and PrI_3 were prepared by direct reaction of the elements as described, purified by vacuum sublimation in contact with only Ta [13], and stored in tightly capped vials in the glovebox. Lanthanum and Pr ($\geq 99.99\%$) were obtained from the Ames Laboratory. The thin, cold-rolled sheets were stored within the glovebox, scraped with a scalpel to remove any surface films (oxides or “tarnish”), and cut into small pieces immediately before use.

For the substitution reaction attempts, typically ~ 0.25 g of reactants (AI_x , R , RI_3) were loaded into Ta tubes that had previously been cleaned, crimped, and welded on one end. Their open ends were then tightly crimped, arc-welded under Ar, and sealed into well-evacuated and baked fused silica jackets before being heated. Reactions of the stoichiometric proportions to yield $\text{NaPr}_6\text{I}_{12}\text{Ir}$, $\text{CaPr}_6\text{I}_{12}\text{Ir}$, $\text{NaLa}_6\text{I}_{12}\text{Fe}$, and $\text{CaLa}_6\text{I}_{12}\text{Co}$ were carried out at 900°C for 2 weeks, followed by cooling at $10^\circ\text{C}/\text{h}$, and these resulted in the formation of the appropriate substitution products in high yield ($\geq 90\%$) judging from relative powder pattern diffraction intensities. Temperatures in the neighborhood of 800°C also were suitable for Na and Ca.

Phases were identified and yields were estimated by visual examination of Guinier powder diffraction patterns of reaction products obtained with the aid of an Enraf-Nonius FR-552 camera and their comparisons with calculated patterns. Relative positions of the indexed diffraction lines of known phases and those of Si (NIST, SRM-640b) as an internal standard were used in the calculation of lattice parameters and their standard deviations via least-squares refinements. Reported data came from powder patterns composed of at least 90% of the target $AR_6I_{12}Z$ -type product (as visually estimated) for which at least 10 sharp, indexed diffraction lines had been matched on individual patterns. In some cases, the parameter errors refined from poorer (fewer) powder data were markedly larger than from the diffractometer, and the latter were used instead. The most common unwanted product observed was crystalline LaOI (or PrOI). This phase appeared in almost every powder pattern, usually in $\leq 10\%$ yield, and presumably arose from adventitious water from the

fused silica when heated or, less likely, oxygen in the Ta tube. No other secondary species was seen.

2.2. Crystallography

Irregular black crystals were mounted in thin-walled glass capillaries with the aid of a small amount of degassed Apiezon L grease, and Laue photos were taken to determine their suitability. Suitable crystals were found for all products except $\text{CaPr}_6\text{I}_{12}\text{Ir}$. Diffraction data for one hemisphere ($\pm h, k, \pm l$) were collected at room temperature up to $2\Theta = 60^\circ$ with the aid of graphite-monochromated $\text{MoK}\alpha$ radiation and a Rigaku AFC6 diffractometer. In all cases, routine indexing and cell reduction readily gave the R -centered hexagonal unit cell of the R_7X_{12} structure. Reflection data were empirically corrected for absorption with the aid of ten ψ -scans except for the Na–Pr–Ir phase [15]. Scans for this crystal were poor, and a cylindrical correction was applied according to shape and dimensions of the crystal. Systematic absences were always consistent with possible space groups $R\bar{3}$ (No. 148), $R3$ (No. 146), and so forth. The structures were solved by direct methods and refined in the expected centrosymmetric group $R\bar{3}$.

3. Results

3.1. Lattice dimensions

Unit cell dimensions of the target compounds as refined from Guinier powder patterns or diffractometer data are listed in Table 1. It has been previously reported that the dimensions of these compounds do not change much as Z is varied within a period as long as

the other elements are held constant [5,6,11]. In this work, both the third-period Z interstitials Fe and Co produced slightly smaller volumes ($12\text{--}28 \text{ \AA}^3$) than their analogues with fifth-period Z (compare $\text{NaLa}_6\text{I}_{12}\text{Os}$, $\text{CaLa}_6\text{I}_{12}\text{Os}$: $V = 2521.8(8)$, $2507.0(2) \text{ \AA}^3$, respectively [11]). As expected, the Pr compounds had $\sim 5\%$ smaller unit cell volumes than analogous La compounds, whereas the Os–Ir change was only $\sim 3 \text{ \AA}^3$ [3,11]. The volume increases from a Na or Ca substitution into these $R_7\text{I}_{12}Z$ in general result mainly from dimensional increases in c as the cavity about $R2$ elongates. Possible variations in the actual A content in these samples have not been considered at this point.

3.2. Single crystal X-ray diffraction

A summary of the loaded and refined compositions and of some crystallographic and refinement parameters for the three refined results are given in Table 2, and the

Table 1
Refined unit cell constants for $AR_6\text{I}_{12}Z$ (\AA , \AA^3)^a

Loaded composition	a	c	V
$\text{NaPr}_6\text{I}_{12}\text{Ir}^b$	15.958(8)	10.841(8)	2391(3)
$\text{CaPr}_6\text{I}_{12}\text{Ir}^b$	15.964(8)	10.813(8)	2386(3)
$\text{Pr}_7\text{I}_{12}\text{Ir}^c$	15.930(2)	10.724(2)	2357.0(6)
$\text{NaLa}_6\text{I}_{12}\text{Fe}^d$	16.142(2)	11.122(2)	2509.7(7)
$\text{CaLa}_6\text{I}_{12}\text{Co}^d$	16.009(2)	11.099(2)	2463.4(7)

^aSpace group $R\bar{3}$ (No. 148), $Z = 3$.

^bLeast-squares refinement of Guinier powder diffraction patterns with Si as an internal standard; $\lambda = 1.540598 \text{ \AA}$, 23°C .

^cRef. [5].

^dDiffractometer indexing of 25 reflections obtained by a random search pattern.

Table 2
Some crystallographic and refinement data for three $AR_6\text{I}_{12}Z$ compounds^a

Composition	$(\text{Na}_{0.90}\text{Pr}_{0.10})\text{Pr}_6\text{I}_{12}\text{Ir}$	$(\text{Na}_{0.954}\text{La}_{0.046})\text{La}_6\text{I}_{12}\text{Fe}$	$(\text{Ca}_{0.801}\text{La}_{0.199})\text{La}_6\text{I}_{12}\text{Co}$
f.w.	2596.8	2440.5	2475.0
Cation compn. loaded	$\text{Na}_{1.0}$	$\text{Na}_{1.0}$	$\text{Ca}_{1.0}$
d_{calc} (g/cm^3)	5.412	4.833	4.965
$\mu(\text{MoK}\alpha)$, mm^{-1}	24.901	18.978	19.541
Crystal dimen. (mm)	$0.10 \times 0.12 \times 0.12$	$0.10 \times 0.09 \times 0.12$	$0.09 \times 0.09 \times 0.12$
No. meas. refl.	3271	3437	3369
No. indep. refl.	1561	1640	1609
$R(\text{int})$ ($I > 0$)	0.234	0.145	0.081
No. obs. refl. ($I \geq 2\sigma_I$)	759	645	960
No. of variables	34	34	34
Rel. transm. coeff.	0.74–1.00	0.375–1.00	0.546–1.00
Extinct. coeff. (10^{-5})	11(4)	1(2)	26.3(1)
Goodness of fit	1.009	0.976	0.989
$R1$, $wR2$ ($I \geq 2\sigma_I$)	0.076, 0.178	0.061, 0.123	0.036, 0.057
$R1$, $wR2$ (all data)	0.170, 0.236	0.205, 0.165	0.099, 0.070
Largest resid. peaks ($\text{e}^-/\text{ \AA}^3$)	5.52 (1.12 \AA from Ir), –7.21 (0.75 \AA from Pr1)	3.37 (3.06 \AA from I1), –2.31 (0.22 \AA from La1)	1.71 (0.6 \AA from I2), –1.63 (0.9 \AA from La1)

^aLattice parameters in Table 1.

Table 3
Parameters for refined $(A_xR_{1-x})R_6I_{12}Z$ structures

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Occ.	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$(Na_{0.90(2)}Pr_{0.10(2)})Pr_6I_{12}Ir$											
Pr1	0.8821(1)	0.0452(1)	0.1509(1)	0.024(1)	1	0.024(1)	0.021(1)	0.027(1)	−0.001(1)	−0.005(1)	0.011(1)
I1	0.8678(1)	0.0513(7)	−0.3326(2)	0.029(1)	1	0.028(1)	0.029(1)	0.028(1)	0.003(1)	−0.006(1)	0.014(1)
I2	0.7465(2)	0.0994(2)	−0.6696(2)	0.035(1)	1	0.046(1)	0.033(1)	0.038(1)	0.009(1)	0.015(1)	0.028(1)
Ir	0	0	0	0.015(1)	1	0.015(1)	U_{11}	0.016(1)	0	0	$\frac{1}{2}U_{11}$
Na	0	0	$\frac{1}{2}$	0.035(7)	0.90(2)	0.032(7)	U_{11}	0.04(1)	0	0	$\frac{1}{2}U_{11}$
Pr2	0	0	$\frac{1}{2}$	0.035	0.10(2)	0.032	U_{11}	0.04	0	0	$\frac{1}{2}U_{11}$
$(Na_{0.954(2)}La_{0.046(2)})La_6I_{12}Fe$											
La1	0.78271(9)	0.28892(8)	0.1857(1)	0.0320(3)	1	0.0334(7)	0.0237(6)	0.0345(6)	0.0030(6)	−0.0104(6)	0.0111(5)
I1	0.84832(9)	0.4643(1)	−0.0009(1)	0.0318(4)	1	0.0342(8)	0.0324(7)	0.0298(6)	0.0066(6)	0.0088(6)	0.0173(6)
I2	0.9211(1)	0.2342(1)	0.0023(1)	0.0381(4)	1	0.0490(9)	0.0365(8)	0.0413(8)	0.0114(7)	0.0148(7)	0.0308(8)
Fe	0	0	0	0.019(1)	1	0.021(2)	U_{11}	0.016(3)	0	0	$\frac{1}{2}U_{11}$
Na	0	0	$\frac{1}{2}$	0.027(5)	0.954(2)	0.030(6)	U_{11}	0.023(8)	0	0	$\frac{1}{2}U_{11}$
La2	0	0	$\frac{1}{2}$	0.027	0.046(2)	0.030	U_{11}	0.023	0	0	$\frac{1}{2}U_{11}$
$(Ca_{0.801(1)}La_{0.199(1)})La_6I_{12}Co$											
La1	0.50445(4)	0.21611(4)	0.18606(4)	0.0166(1)	1	0.0154(2)	0.0162(3)	0.0179(2)	0.0008(2)	−0.0001(2)	0.0076(2)
I1	0.61596(5)	0.15187(4)	−0.00709(5)	0.0238(2)	1	0.0248(3)	0.0256(4)	0.0212(3)	−0.0054(2)	−0.0022(2)	0.0128(3)
I2	0.42970(6)	0.01851(5)	0.33688(6)	0.0338(2)	1	0.0328(4)	0.0169(3)	0.0378(4)	0.0078(3)	0.0121(3)	0.0021(3)
Co	0	0	0	0.0124(6)	1	0.0115(8)	U_{11}	0.014(1)	0	0	$\frac{1}{2}U_{11}$
Ca	0	0	$\frac{1}{2}$	0.039(1)	0.801(1)	0.030(2)	U_{11}	0.059(3)	0	0	$\frac{1}{2}U_{11}$
La2	0	0	$\frac{1}{2}$	0.039	0.199(1)	0.030	U_{11}	0.059	0	0	$\frac{1}{2}U_{11}$

Table 4
Selected interatomic distances for $(A_xR_{1-x})R_6I_{12}Z$ (Å)

Atoms\comp.	$(Na_{0.90}Pr_{0.10})Pr_6I_{12}Ir$	$(Na_{0.954}La_{0.046})La_6I_{12}Fe$	$(Ca_{0.801}La_{0.199})La_6I_{12}Co$
Z–R1	2.844(2)	2.840(2)	2.8397(3)
A/R2–I1	3.185(2)	3.1395(9)	3.1426(7)
R1–I2 ^a	3.191(2)	3.244(2)	3.233(1)
R1–I2 ^a	3.209(2)	3.246(2)	3.2336(9)
R1–I2 ^b	3.330(2)	3.449(2)	3.3910(9)
R1–I1	3.167(2)	3.232(2)	3.2675(9)
R1–I1	3.176(2)	3.240(2)	3.2745(9)
R1–R1 ^c	4.014(3)	4.012(2)	4.010(1)
R1–R1	4.031(3)	4.019(2)	4.022(1)
I1–I1 ^d	4.301(2)	4.408(2)	4.339(1)

^aWaist-bridging iodine.

^bExo bonding function.

^cNormal to ϵ .

^dShortest I–I contact.

resultant atom positions and anisotropic displacement parameters are listed in Table 3. Important interatomic distances are reported in Table 4. The atom numbering scheme is identified in Fig. 2.

3.2.1. $(Na_{0.90(2)}Pr_{0.10(2)})Pr_6I_{12}Ir$

Isotropic refinement of the isolated position at 0, 0, $\frac{1}{2}$ as only Na gave R1, wR2 values of 13.8%, 22.4% and a relatively small value of U_{eq} . Isotropic refinement when a second Pr atom was assigned to share the position with Na (with U_{eq} for both constrained to the same value) resulted in smaller residuals and occupancies of 90(2)% Na, 10(2)% Pr, with U_{eq} the same as or only slightly greater than the average of the others. Although some

refinement criteria are not as good as those usually attained, probably because of a limited quality absorption correction, standard deviations in positions and distances are acceptable.

3.2.2. $(Na_{0.954(2)}La_{0.046(2)})La_6I_{12}Fe$

Isotropic refinement of only Na on the site gave R1, wR2 values of 10.3%, 25.3%. A second La atom assigned to share the site with Na (with the same U_{eq}) gave reduced residuals and refined occupancies of 95.4(2)% Na, 4.6(2)% La, the U_{eq} for this site being slightly less than the (relatively large) average of the others.

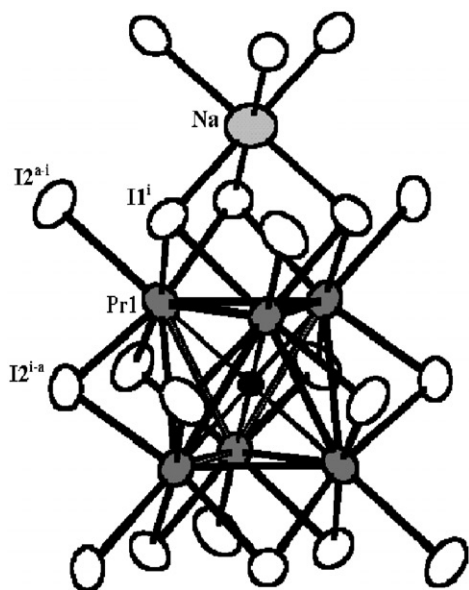


Fig. 2. One independent cluster unit in $\text{Na}_{0.90}\text{Pr}_{0.10}(\text{Pr}_6\text{I}_{12}\text{Ir})$ with the atom identifications. I, Pr, Ir atoms are white, gray and black, respectively; the substitution site for Na(Pr) is larger and light gray (90% probability).

3.2.3. $(\text{Ca}_{0.801(1)}\text{La}_{0.199(1)})\text{La}_6\text{I}_{12}\text{Co}$

Isotropic refinement of the isolated position as only La resulted in $R1$, $wR2$ values of 11.8%, 34.0% with U_{eq} twice as large as the average of the others. On the other hand, isotropic refinement of the position as only Ca gave $R1$, $wR2$ values of 9.9%, 28.1% with a U_{eq} value comparable to the others. Further, isotropic refinement of a second La (with equal U_{eq}) to share the position resulted in smaller residuals and occupancies of 80.1(1)% Ca and 19.9(1)% La with U_{eq} similar to those for other atoms.

4. Discussion

In a more general view, the single crystal X-ray diffraction results here agree with other recent findings [11], namely, that Na or Ca atoms will substitute for the isolated lanthanide atoms to form $AR_6I_{12}Z$ phases without destruction of the $R_7X_{12}Z$ structure type (Fig. 1). Mixed occupancies were also established for some of the earlier examples after less A was loaded. Here, essentially all of the loaded A substitutes for $R2$ in the parent structure, more so with sodium, but in other cases a small residual of $R2$ remains for reactions loaded $A_1R_6I_{12}\text{Os}$, 5–10% with Na, 20% with Ca [11]. In some cases, the displacement parameters for the smaller cations are somewhat larger than those for the other atoms, but this is not unusual for alkali- or alkaline-earth-metal cations in such voids [5,6,11].

The sum of crystal radii for six-coordinate A cations and iodide in these structures are always within about

0.05 Å of the observed $A-I$ distances, Table 4 [16]. Coincidentally, the $R-Z$ distance is constant in this series when Pr with Ir is switched to La with Fe or Co. The $d(R-I)$ and $d(R-R)$ differences are entirely normal save for $d(A/R-I)$. Here, $d(\text{Na}/\text{Pr}-\text{I}1)$ seems to be an unexpectedly ~ 0.04 Å larger than $d(\text{Na}/\text{La}-\text{I}1)$, but this in fact appears to be a reflection of a secondary effect as I1 moves closer to the metal site Pr1 with its higher effective charge/bond strength. There seems to be no significant difference when R is changed from La to Pr or Z is changed from Os, Ir to Fe or Co. Although isotypic rhombohedral $\text{Zr}_6\text{I}_{12}\text{Z}$ phases are known without the isolated cation [2], the cation-free lanthanide analogues have never been prepared, probably because the cluster products would be quite electron-deficient.

Relative values achieved for x in $(A_xR_{1-x})R_6I_{12}Z$ syntheses are more difficult to interpret. The A coefficients of 0.90 and 0.94 for Na and 0.80 for Ca in different hosts when loaded with the stoichiometric amounts of A (Table 3) compare with 1.00 for Na or Sr and 0.91 for Ca in parallel reactions loaded near a $A_2\text{La}_6\text{I}_{12}\text{Os}$ composition [11]. All are clearly higher than for the troublesome $\text{Ca}_{0.65(1)}\text{Pr}_{0.35(1)}\text{Pr}_6\text{I}_{12}\text{Co}$ reported earlier [5] for which approximations in the refinement of a data set from a twinned crystal ($\sim 22\%$ reverse component) may have introduced some additional error. The synthetic conditions were otherwise quite similar; although it is noteworthy that the particular parent phases $\text{Pr}_7\text{I}_{12}\text{Fe}$ and $\text{Pr}_7\text{I}_{12}\text{Co}$ were produced only in poor yields in the earlier study, in contrast to the lanthanum analogues here. Also, lattice dimensional data for the Ca–Gd–Co product suggested that a limited reaction had occurred because of only a small (5%) change in lattice volume from $\text{Gd}_7\text{I}_{12}\text{Co}$, whereas Ca–Gd–Fe yielded the only known example with a substantial (11.5%) decrease in cell volume from that of the corresponding $\text{Gd}_7\text{I}_{12}\text{Fe}$.

In any case, it is not appropriate to attempt to interpret differences in x among the nine substitution results among $(A_xR_{1-x})R_6I_{12}Z$ phases solely in terms of changes imagined in the “stability” of only the substituted products. Rather, it should be noted that either less or completely unsuccessful reactions that had been loaded as $AR_6I_{12}Z$ yielded AI or AI_2 plus $R_6I_{10}Z$ as the major alternate products. Thus, it is actually the relative stabilities of the target phases vs these alternatives and their dependancies on A , R , and Z that govern the degree of success, and this is clearly a much more complex matter. As noted before [11], the magnetic properties of clusters with different formal electronic counts are not classical or simple, so that electronic contributions to stability are not readily interpretable.

Notwithstanding, the opportunity to substitute some heteroatoms for the isolated $R2$ atom in all examples of the classic $R_7X_{12}Z$ structure does give us data with

which to define some general structural characteristics and problems associated with this structure type. In particular, further possible variations in the size of the encapsulated Z relative to the nature of both R and X also contribute some generic features, at least in a qualitative sense, as follows.

Among the earliest $R_7X_{12}Z$ phases characterized structurally were those with small Z and R with larger halide. Interestingly, the three phases characterized structurally among $Sc_7(Br,I)_{12}(B,C)$ were found to occur in the acentric space group $R\bar{3}$, with the isolated Sc2 atoms displaced $\sim 0.5 \text{ \AA}$ from the centers of the X_1 antiprisms [4]. There was no evidence of twinning, and only very small electron density residuals remained. Somewhat less extreme size differences with chloride in $Sc_7Cl_{12}(B,N)$ afforded the much more common $R\bar{3}$ result, but even here a considerable elongation of the anisotropic displacement of Sc2 along c was evident [3]. These effects appear to have some of the pathology associated with “matrix effects” brought on by close-packing of halogen atoms (ions) among which some octahedral cavities are occupied by small R and others, by small Z , especially when X is large. Other more or less simultaneous studies of $R\bar{3}$ “ R_7I_{12} ” phases for $R = \text{La–Lu}$ were made on compounds that were later concluded to be stabilized by impurities Z , probably small carbon atoms [1]. These exhibited similarly elongated R_2 ellipsoids (U_{33}/U_{11} between ~ 3 and 9), for which disorder of antiphase domains made up of acentric building blocks with displaced R_2 atoms was considered possible. But structural studies of this group of iodides with larger R were also materially troubled by substantial twinning which, when untreated, gave rise to extra electron density that fell in both normal cavities and on other atoms, including the interstitial. Interestingly, the only other examples of recognized twinning (or extra electron density in X_6 cavities) in this structure type evidently occurred in the work that prompted this study, $(\text{Ca}_x\text{Pr}_{1-x})\text{Pr}_6\text{I}_{12}\text{Co}$ (above) [5]. Here the halogen was again large and in the Gd study, which also exhibited some troubled results, the cation was a little smaller. The Ca substitutions attempted earlier in the $\text{Gd}_7\text{I}_{12}M$ hosts, $M = \text{Fe, Co}$, were the major instances to date in which ΔV_{cell} was about zero or negative ($M = \text{Fe}$). (In another instance, $\Delta V_{\text{cell}} \sim 0$ for $\text{MgLa}_6\text{I}_{12}\text{Os}$, but this has been characterized only via powder data [11].) Otherwise, substitutions to gain $AR_6\text{I}_{12}Z$ phases with transition metal Z generally result in volume increases, particularly via an expansion along c , and for the eight examples that have been well defined structurally, no twinning or R_2 ellipsoidal troubles. In other words, iodide examples containing larger transition metal interstitials in R_6Z clusters are crystallographically better behaved than when R_6Z contains a small and more electronegative B or C atom. The latter were noted to also be distinctly more polar [1].

When R and Z are both small (Sc, C), structural distortions become noticeable with all X .

5. Conclusions

Four new examples of quaternary lanthanide halide cluster compounds $A(\text{La,Pr})_6\text{I}_{12}Z$ with transition metal interstitials (Z) and Na^+ or Ca^{2+} cations (A) have been synthesized by high temperature solid state techniques in the rhombohedral structure type known for many other $R(R_6X_{12}Z)$ phases. Single crystals obtained from nominal $\text{NaPr}_6\text{I}_{12}\text{Ir}$, $\text{NaLa}_6\text{I}_{12}\text{Fe}$, and $\text{CaLa}_6\text{I}_{12}\text{Co}$ compositions were structurally characterized to show that these alkali-or alkaline-earth-metal cations displace 80–95% of the R_2 position halfway between R_6Z clusters along c . Some broader generalities regarding structural distortions in $R(R_6X_{12}Z)$ systems can also be identified. The ideality of all examples of this structure type is better for the larger Z when R is large.

6. Uncited reference

[14].

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