

Thermopower enhancement by encapsulating cerium in clathrate cages

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I. SINGLE CRYSTAL X-RAY DIFFRACTION

A. Experimental details

Single crystal data collection was performed on a Bruker APEX2 four-circle diffractometer in Kappa geometry using a CCD detector for the sample Ce-BAS and on a Stoe StadiVari four-circle diffractometer with an open Eulerian cradle in combination with a Dectris PILATUS 300K pixel detector for the sample La-BAS. For both samples complete reciprocal spheres with high redundancy were measured using laboratory X-ray sources. The data set for Ce-BAS was corrected for absorption using a semi-empirical absorption correction by applying the multi-scan approach of SADABS¹. A numerical absorption correction was applied using the program HABITUS² for the La-BAS data set. Extinction correction was applied based on the B_C type 1 Gaussian model³ within the refinement program JANA2006⁴. Further details of the data collection and refinements are summarized in Table I - V.

Different models for the partial replacement of Ba with Ce on the $2a$ and $6d$ crystallographic site, within the small and large cage, respectively, were refined using the program JANA2006⁴. Due to the close X-ray contrast from Ba and Ce (La) we fixed the Ba to Ce (La) ratio to the value determined by EXD. The model for the partial Ba replacement by Ce on the $2a$ site resulted in the residuals $R = 1.90\%$ and $R = 2.61\%$, the model with Ce

on the $6d$ site yields $R = 1.99\%$ and $R = 3.1\%$ for Ce-BAS and La-BAS, respectively. The Fourier maps for refinement cycles with 6 Au atoms on the $6c$ site resulted in a negative electron density on the $6c$ site and a positive one on the $24k$ site of Si. The redistribution of some Au atoms on the $24k$ site with a concomitant distribution of Si on the $6c$ site give a significant residual reduction to $R = 1.74\%$ for Ce-BAS and $R = 2.18\%$ La-BAS.

B. Results

Our single crystal X-ray refinements yield the lattice parameters $a = 10.3950(1) \text{ \AA}$ and $a = 10.3954(4) \text{ \AA}$ for Ce-BAS and La-BAS, respectively. These are sizeably smaller than published values for $\text{Ba}_8\text{Au}_x\text{Si}_{46-x}$ (BAS) clathrates with similar Au content^{5-7,11}. The structural features of the framework of our clathrates are similar to those of BAS. The $6c$ position is shared by Au and Si although a small portion of Au (2%) occupies the $24k$ site of Si, a feature which was also found in BAS^{5,7}. No appreciable improvement of the refinement was obtained by introducing vacancies. Because of the very similar atomic form factors of Ba and Ce (La) for X-ray scattering, no partition in $2a$ and $6d$ sites could be found. Nevertheless, a specific location of Ce (La) can be uncovered indirectly. The introduction of smaller Ce and La atoms results not only in a unit cell reduction but also in local lattice distortions. At the general unit cell contraction by about 0.2% the radius of the smaller cage reduces by 0.81% in Ce-BAS and by 0.89% in La-BAS, whereas that of the larger cage remains essentially unchanged. This fact is strong evidence of a preferential location of Ce (La) in the smaller cages. This is consistent with the occupation of the smaller cages in mixed Ba-Eu clathrates by Eu, which could be obtained directly from X-ray refinements^{8,9} since the difference in the Ba and Eu atomic form factors is essential.

The high quality of our refinements attested by the low R values resulted in substantially smaller atomic displacement parameters (ADPs) in comparison with earlier investigations^{7,10}. For u_{22} on $6d$ (Ba in large cage) and u_{22} on $6c$ (Au/Si in large cage), however, this reduction is smaller than the average value, both in Ce-BAS and La-BAS. This may be a sign of enhanced rattling of Ba in the large cages. An even more important issue, however, is to analyze the ADPs in the small cages where Ce (La) are situated. For Ce-BAS, u_{11} on $2a$ (Ce/Ba in small cage) is likewise reduced by less than the average value. For La-BAS, however, u_{11} on $2a$ (La/Ba in small cage) is reduced by the average value.

However, even this maintenance of u_{11} on $2a$ after the substantial (unproportional) cage shrinkage indicates an effectively enhanced rattling. Moreover, $2a$ is shared by Ce (La) and Ba, and u_{11} is merely an average value. The shrinking of the small cages results inevitably in the reduction of the rattling amplitude of Ba and hence an enhancement of the rattling amplitude of Ce (La).

C. Calculation of the mean cage radius

We calculated the cage radii of the two clathrate cages by

$$R_{\text{cage}} = \frac{\sum_{i=1}^N R_i}{N} \quad (1)$$

where N is the number of cage atoms (20 for the small cage, 24 for the large cage) and R_i are distances from the i -th cage atom to the cage center.

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TABLE I: Crystal data.

Crystal data	Ce-BAS	La-BAS
Refined chemical formula ¹	Ba _{6.91} Ce _{1.06} Au _{5.75} Si _{40.2}	Ba _{6.99} La _{1.23} Au _{5.92} Si _{39.01}
Formula weight (g mol ⁻¹)	3389.77	3422.2
Crystal system	cubic	cubic
Space group	<i>Pm</i> $\bar{3}$ <i>n</i>	<i>Pm</i> $\bar{3}$ <i>n</i>
Unit cell dimensions (Å)	10.3950(1)	10.3954(4)
Unit cell volume (Å ³)	1123.24(3)	1123.37(6)
<i>Z</i>	1	1
Calculated density D_x (g cm ⁻³)	4.9373	5.0118
Absorption coefficient (mm ⁻¹)	26.168	27.238
Crystal shape	irregular	irregular
Crystal dimensions (μ m)	60 \times 20 \times 10	40 \times 40 \times 5

¹Ba, Ce (La) content fixed to EDX results

TABLE II: Data collection.

Data collection	Ce-BAS	La-BAS
Diffractometer	Bruker D8/APEXII	STOE StadiVari
Detector	CCD	Dectris Pilatus 300k
Data collection method	ϕ scans	ϕ scans
Temperature (K)	295	295
Radiation (Å)	Mo K α	Mo K α
θ_{\max} (°)	50.12	39.94
No. collected reflections ($I > 3\sigma(I)$)	38782	8137
No. independent reflections	1097	612
No. observed reflections	975	432
$R_{(\text{int})}$ (%)	6.43	7.20

TABLE III: Refinement.

Data collection	Ce-BAS	La-BAS
Absorption correction	Multi-scan <i>SADABS</i> ¹	Numerical <i>HABITUS</i> ²
Extinction correction	B-C type 1 Gaussian isotrop ³	B-C type 1 Gaussian isotrop ³
No. refined parameters	19	19
Weighting scheme	based on measured s.u.s, $w = 1[\sigma^2(F) + 0.0001 (F^2)]$	based on measured s.u.s, $w = 1[\sigma^2(F) + 0.0001 (F^2)]$
$R[F > 3\sigma(F^2)]$ (%)	1.74	2.18
$wR(F^2)$ (%)	2.31	2.61
S	1.64	1.38
$\Delta\sigma_{\max}$ (e Å ⁻³)	1.91	2.62
$\Delta\sigma_{\min}$ (e Å ⁻³)	-2.1	-1.22

TABLE IV: Site occupancies, atomic coordinates and displacement parameters (\AA^2).

	Ce-BAS	La-BAS
Wyckoff site (2a): $(0, 0, 0)^1$; $(2 - m)$ Ba; (m) Ce (La)		
m	0.132	0.149
$u_{\text{iso};\text{Ba,Ce(La)}}$	0.00677(4)	0.00426(9)
$u_{11;\text{Ba,Ce(La)}}$	0.00678(11)	0.00426(29)
Wyckoff site (6d): $(0.25, 0.5, 0)^2$; (6) Ba		
$u_{\text{iso},\text{Ba}}$	0.01606(7)	0.01281(20)
$u_{11,\text{Ba}}$	0.01038(16)	0.00745(59)
$u_{22,\text{Ba}}$	0.01890(14)	0.01548(42)
Wyckoff site (6c): $(0.25, 0, 0.5)^2$; (6) Au		
$u_{\text{iso};\text{Au,Si}}$	0.00648(3)	0.00484(13)
$u_{11;\text{Au,Si}}$	0.00677(8)	0.00428(20)
$u_{22;\text{Au,Si}}$	0.00660(6)	0.00479(33)
Wyckoff site (16i): $(x, x, x)^3$; (16) Si		
x	0.1832(1)	0.1830(1)
$u_{\text{iso},\text{Si}}$	0.00559(8)	0.00436(23)
$u_{11,\text{Si}}$	0.00562(26)	0.00436(69)
$u_{23,\text{Si}}$	-0.00058(8)	-0.00051(50)
Wyckoff site (24k): $(0, y, z)^4$; $(24 - 0)$ Si; (0) Au		
0	0.418(3)	0.312(1)
y	0.3041(1)	0.3037(2)
z	0.1174(1)	0.1170(2)
$u_{\text{iso};\text{Si,Au}}$	0.00667(6)	0.00479(68)
$u_{11;\text{Si,Au}}$	0.00677(33)	0.00428(90)
$u_{22;\text{Si,Au}}$	0.00660(33)	0.00479(88)
$u_{33;\text{Si,Au}}$	0.00642(32)	0.00531(95)
$u_{23;\text{Si,Au}}$	-0.00012(21)	-0.00011(88)

$$^1u_{11} = u_{22} = u_{33}; u_{23} = u_{13} = u_{12} = 0; ^2u_{22} = u_{33}; u_{23} = u_{13} = u_{12} = 0$$

$$^3u_{22} = u_{33}; u_{23} = u_{13} = u_{12}; ^4u_{13} = u_{12} = 0$$

TABLE V: Selected interatomic distances (Å).

	Ce- BAS	La- BAS
$\text{Au}_{6c} - \text{Ba}_{6d}^{(i),(ii),(iii)}$	3.6752(3)	3.6753(2)
$\text{Au}_{6c} - \text{Si}, \text{Au}_{24k}^{(iv),(v),(vi)}$	2.4607(8)	2.4650(2)
$\text{Ba}, \text{La}(\text{Ce})_{2a} - \text{Si}, \text{Au}_{24k}^{(ii),(vii),(viii),(ix),(x),(xi),(xii),(xiii),(xiv),(xv),(xvi)}$	3.3870(8)	3.3830(2)
$\text{Ba}_{2a} - \text{Si}_{16i}^{(vii),(viii),(ix),(xvii),(xviii),(xix),(xx)}$	3.2993(6)	3.2956(15)
$\text{Ba}_{6d} - \text{Si}_{24k}^{(vi),(v),(x),(xviii),(xxi)}$	3.5201(5)	3.5210(17)
$\text{Si}_{16i} - \text{Si}_{16i}^{(xxi)}$	2.4037(9)	2.411(2)
$\text{Si}_{16i} - \text{Si}, \text{Au}_{24k}^{(ii),(x)}$	2.3820(8)	2.380(2)
$\text{Si}, \text{Au}_{24k} - \text{Si}, \text{Au}_{24k}^{(ix)}$	2.4382(1)	2.433(4)

Symmetry codes:

- $(i) - x + 1, -y + 1, z; (ii) y, z, x;$
- $(iii) - y + 1, z, -x; (iv) - x + 1, y, -z;$
- $(v) z + 1/2, -y + 1/2, x - 1/2; (vi) - z + 1/2, -y + 1/2, -x + 1/2;$
- $(vii) - x, -y, z; (viii) - x, y, -z;$
- $(ix) x, -y, -z; (x) z, x, y;$
- $(xi) z, -x, -y; (xii) - z, -x, y;$
- $(xiii) - z, x, -y; (xiv) - y, z, -x;$
- $(xv) y, -z, -x; (xvi) - y, -z, x;$
- $(xvii) - x, -y, -z; (xviii) x, y, -z;$
- $(xix) x, -y, z; (xx) - x, y, z; (xxi) z, -x + 1, -y$