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Re-investigation of the crystal structure of trieuropium octagallide, $Eu_{3-x}Ga_{8+3x}$ (x = 0.12)

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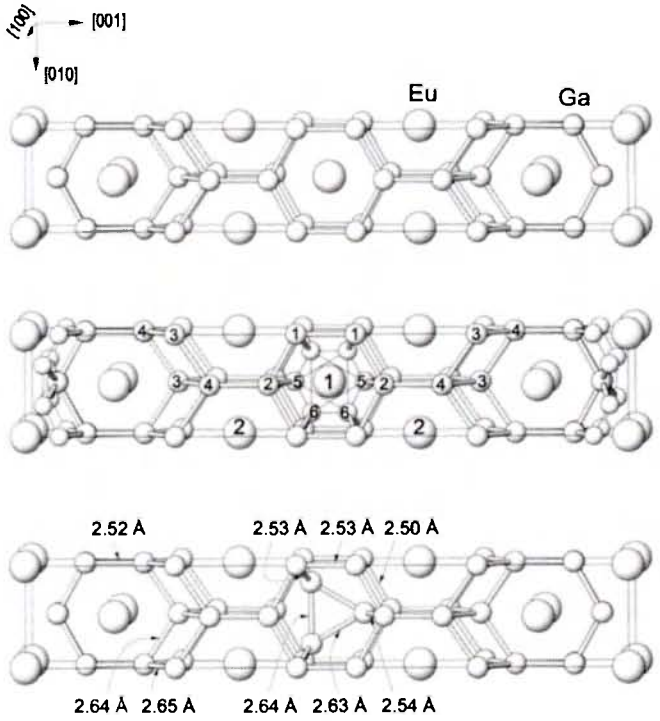

Abstract

$Eu_{2.88}Ga_{8.36}$, orthorhombic, *Immm* (no. 71), a = 4.4105(3) Å, b = 4.3732(2) Å, c = 25.852(1) Å, V = 498.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.025, $wR_{ref}(F)$ = 0.062, T = 295 K.

Source of material

Several samples with the nominal composition Eu_xGa_{100-x} ($23 < x < 28$) were prepared from the elements: Eu, 99.9 % (Lamprecht, additionally distilled); Ga, 99.9999 % (Chempur). The mixtures of the appropriate amounts of the starting components were closed in Ta crucibles under an argon pressure of about 800 mbar. Each tantalum tube was subsequently sealed into a silica ampule to prevent oxidation of tantalum at high temperatures. The synthesis was performed by heating (2 K/h) of the reaction mixtures up to 950-1000 °C, annealing at these temperatures for 2 h, slow cooling the temperature (within 6 days) to 600 °C, subsequent thermal treatment for 2 weeks and quenching in cold water. Alternatively, the reported phase can be obtained by high-frequency melting of the elements in an open glassy carbon crucible under an argon atmosphere with subsequent homogenization at 600 °C. Platelet-like single crystal was mechanically extracted from annealed sample with the composition $Eu_{26}Ga_{74}$.

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Experimental details

The unit cell parameters were obtained from least-squares refinement of 35 reflections taken from a Guinier powder pattern (Huber G670 camera, Cu$K_{\alpha 1}$ radiation, λ = 1.54056 Å) using germanium (a = 5.657906 Å) as an internal standard.

Discussion

The crystal structure of Eu_3Ga_8 was primarily investigated by X-ray powder diffraction methods [1,2] and was found to be a binary representative of the $U_3Ni_4Si_4$ structure type [3] (figure, top). Despite the acceptable interatomic distances, the residual values were relative high (R_I = 0.15 [1] and R_I = 0.11 [2]) and atomic displacement factors revealed unusual behavior deviating from the values expected for the respective atomic masses. These contradictions were the reason for crystal structure re-investigation using single crystal data.

Detailed analysis of the difference Fourier maps revealed, beside the known europium and gallium positions, additional electron density maxima in the vicinity of the Eu1 atoms with the AlB_2-like gallium environment (figure, middle), as this was found for the $Eu_{1-x}Ga_{2+3x}$ phase [4]. Excluding the forbidden short interatomic distances, the final model of the crystal structure reveals a replacement of a part of europium atoms by triangles of gallium (figure, bottom). Preliminary phase equilibria investigations in the gallium-rich region showed the congruent formation of $Eu_{3-x}Ga_{8+3x}$ at 971 °C. Determination of lattice parameters reveals that the homogeneity range of $Eu_{3-x}Ga_{8+3x}$ at 600 °C extends from x = 0.12 to x = 0.23: a = 4.3991(6) Å – 4.4103(8) Å, b = 4.3841(6) Å – 4.3737(7) Å, c = 25.864(3) A – 25.857(4) A. A similar structural behavior was found for $Sr_{3-x}Ga_{8+3x}$, x = 0.15 [5].

Table 1. Data collection and handling.

Crystal:	metallic platelet, size 0.010 × 0.030 × 0.045 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	411.8 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, φ/ω
$2\theta_{max}$:	64.44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2176, 509
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 485
$N(param)_{refined}$:	35
Programs:	WinCSD [6], ATOMS [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
Ga(5)	4*i*	0.053(1)	0	0	0.0575(9)	0.015(4)
Ga(6)	8*l*	0.058(1)	½	0.198(4)	0.4696(5)	0.014(2)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu(1)	2*a*	0.878(5)	0	0	0	0.0094(4)	0.0125(4)	0.0120(4)	0	0	0
Eu(2)	4*j*		½	0	0.35082(2)	0.0098(3)	0.0109(2)	0.0121(2)	0	0	0
Ga(1)	8*m*	0.5	0.0274(8)	0	0.45111(5)	0.0119(7)	0.0100(5)	0.0083(4)	0	−0.0011(8)	0
Ga(2)	8*m*	0.5	0.4686(7)	0	0.09554(5)	0.0114(7)	0.0095(5)	0.0090(5)	0	0.0002(7)	0
Ga(3)	4*i*		0	0	0.24988(4)	0.0111(5)	0.0127(5)	0.0104(4)	0	0	0
Ga(4)	4*j*		½	0	0.19271(4)	0.0117(5)	0.0128(5)	0.0093(4)	0	0	0

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