Refinement of the crystal structure of europium digallide, $EuGa_2$

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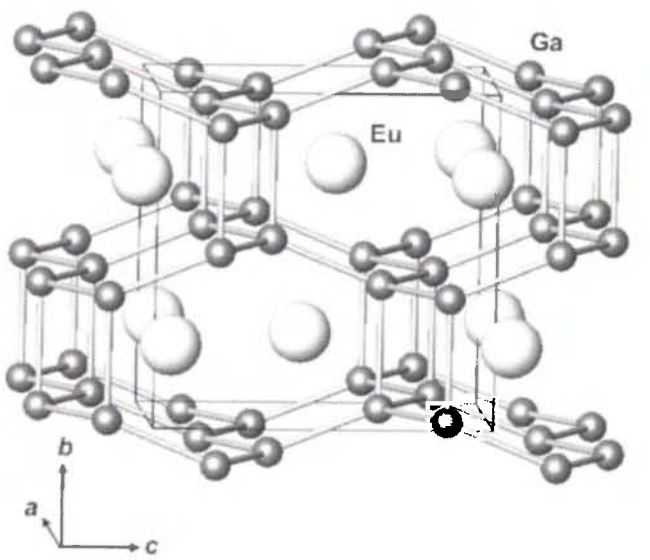

Abstract

$EuGa_2$, orthorhombic, *Imma* (no. 74), a = 4.6459(3) Å, b = 7.6255(5) Å, c = 7.6379(3) Å, V = 270.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.017, $wR_{ref}(F)$ = 0.023, T = 293 K.

Source of material

A series of samples with nominal compositions Eu_xGa_{100-x} ($27 < x < 40$) was prepared by melting of elemental components in a high frequency furnace (open carbon crucible; argon atmosphere; europium, 99.9 %, Lamprecht, additionally distilled; Ga, 99.9999 %, Chempur). For homogenization, the samples were wrapped in Mo foil, sealed into argon filled (400 mbar) silica tubes, annealed for 500 h at 600 °C and finally quenched in cold water. Single crystals with metallic luster were extracted from the compact alloy with nominal composition $Eu_{33}Ga_{67}$.

Experimental details

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

Discussion

Europium digallide was initially found to have the hexagonal structure of the AlB_2 type [1,2]. Further investigations showed the orthorhombic structure of the KHg_2 type [3,4]. The phase with the crystal structure of the AlB_2 type was explained either to be a high-temperature modification [3] or to be stabilized by impurities [4]. The present investigation confirmed the orthorhombic crystal structure of the KHg_2 type reported earlier from X-ray powder data [3,4]. Our investigations showed that the phase with the KHg_2 atomic arrangement is formed only at stoichiometric ratio of the components (1:2). Slight deviations from the ideal composition ($Eu_{28-30}Ga_{72-70}$) lead to the formation of the phase with AlB_2 structure [5]. The four-bonded gallium atoms in the crystal structure of $EuGa_2$ form slightly puckered hexagonal nets with Ga—Ga distances of 2.653(1) Å and 2.6921(6) Å. The distance between the nets is slightly longer 2.811(1) Å. The europium atoms have coordination number 16 with 12 Ga and 4 Eu neighbors. The Eu—Ga distances cover a narrow range of 3.1474(6) Å – 3.4547(6) Å. Rare earth digallides adopt predominately the AlB_2 type of structure at ambient conditions [6]. Beside the reported phase, only $TmGa_2$ and $LuGa_2$ crystallize with KHg_2 type [7]. As unique representative of this series, $YbGa_2$ adopts the hexagonal $CaIn_2$ structure type at ambient conditions [1,8].

Table 1. Data collection and handling.

Crystal:	silver-metallic, prism-like, size 0.021 × 0.049 × 0.083 mm
Wavelength:	Ag K_α radiation (0.56087 Å)
μ:	227.6 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	47.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1750, 1750
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 255
$N(param)_{refined}$:	12
Programs:	WinCSD [9], ATOMS [10]

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu	4*e*	0	¼	0.04762(7)	0.0070(3)	0.0059(3)	0.0084(3)	0	0	0
Ga	8*i*	0	0.43435(1)	0.66088(1)	0.0066(4)	0.0084(4)	0.0065(4)	0	0	–0.0005(3)

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Crystal structure of dieuropium trigallium iridium, Eu_2Ga_3Ir

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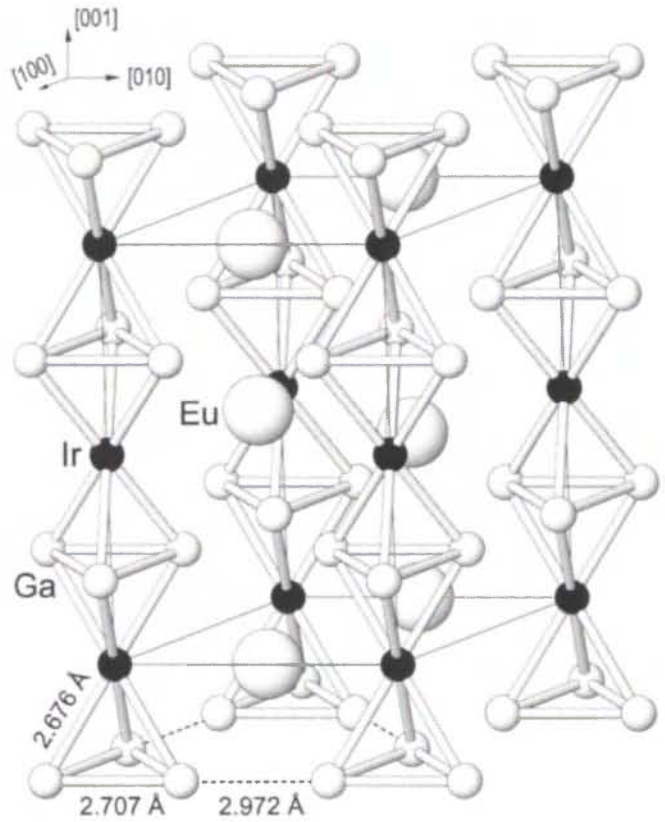

Abstract

Eu_2Ga_3Ir, hexagonal, $P6_3/mmc$ (no. 194), a = 5.6785(2) Å, c = 8.6911(5) Å, V = 242.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.032, $wR_{ref}(F)$ = 0.028, T = 293 K.

Source of material

Starting materials for the preparation (total sample mass 1 g) were ingots of europium (Hunan Institute of Rare Earth Metal Materials, 99.9 %), gallium lumps (Chempur, 99.999 %) and iridium foil (Lamprecht, 99.9 %). Europium was redistilled in vacuum before using. The elemental components were mixed in stoichiometric ratio and sealed into a tantalum tube under an argon pressure of about 800 mbar. The tantalum tube was subsequently closed in a silica ampule to prevent oxidation of tantalum at high temperatures. The synthesis was performed by slow heating of the reaction mixture to 900 °C, annealing for 48 h, lowering the temperature (2 K/h) to 600 °C, annealing for 2 weeks and quenching in cold water. A platelet-like single crystal was mechanically extracted from annealed sample with stoichiometric composition.

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Experimental details

Lattice parameters were obtained by least-squares fitting of 29 reflections extracted from X-ray powder diffraction Guinier data using $CoK_{\alpha 1}$ radiation (λ = 1.788965 Å) and LaB_6 as the internal standard (a = 4.15692 Å).

Discussion

The crystal structure of Eu_2Ga_3Ir adopts Mg_2Cu_3Si type [1] realizing an ordered variant of the hexagonal Laves phase $MgZn_2$ [2-4]. Europium atoms occupy positions of Mg species (4*f*), gallium and iridium are located in the 6*h* and 2*a* sites, respectively. The title compound is the first gallium representative reported with an ordered distribution of atoms on the zinc positions of the aristotype. The environment of each atom has the shape of a Frank-Kasper polyhedron with 16 (4 Eu + 3 Ir + 9 Ga), 12 (6 Ga + 6 Eu) and 12 (6 Eu + 2 Ir + 4 Ga) atoms in the coordination shells of Eu, Ir and Ga, respectively. The interatomic distances d(Eu—Ir) = 3.3099(2) Å, d(Eu—Ga) = 3.138(2) Å, d(Ir—Ga) = 2.676(2) Å and d(Ga—Ga) = 2.707(4) Å are comparable with the sum of the respective atomic radii (r(Eu) = 1.984 Å, r(Ir) = 1.357 Å, r(Ga) = 1.351 Å [5]). On the other hand, Eu—Eu distances (3.4024(4) Å and 3.436(2) Å) are considerably shorter as usually observed in the intermetallic compounds with europium in the $4f^7$ configuration (Eu^{+2}) [6,7]. Similar close Eu—Eu contacts also were observed in the isotypic europium indides $EuIn_{1.28}Pd_{0.72}$ and $EuIn_{1.44}Pt_{0.56}$ [8]. The gallium and iridium species form rows of face- and corner-sharing tetrahedra along the *c* axis. The distances within these tetrahedra of d(Ir—Ga) = 2.676(2) Å and d(Ga—Ga) = 2.707(4) Å are considerably shorter as Ga—Ga interactions between the chains of 2.972(4) Å, so that we suggest an one-dimensional character of [IrGa] polyanion in the Eu_2Ga_3Ir structure, contrary to the usual interpretation of the Laves phases.

In the early work [9], it was shown that, additionally to the size effect in the Laves phases, a low valence electron concentration (VEC) stabilizes the formation of the alloys with cubic $MgCu_2$ (C15) structure [10], the alloys with the high electron concentration crystallize with the hexagonal $MgZn_2$ atomic arrangement (C14). This agrees very well for the pseudobinary $EuIr_2$–$EuGa_2$ system. Whereas the binary $EuIr_2$ compound ([11], low VEC) adopts the $MgCu_2$ structure, Eu_2Ga_3Ir (higher VEC) crystallizes in the hexagonal C14 type.

At the temperatures 90 K < T < 400 K, the susceptibility ($\mu_0(H)$ = 1 T) follows a Curie-Weiss law with an effective magnetic moment μ_{eff} = 8.18 μ_B/Eu-atom and Θp = +3.6(1) K. The effective moment indicates that Eu is in the $^8S_{7/2}$ ground state of the $4f^7$ configuration (Eu^{2+}). Electrical resistivity data indicate metallic conduction in Eu_2Ga_3Ir with ρ (300 K) approx. 150 $\mu\Omega$ cm and ρ_0 approx. 50 $\mu\Omega$ cm. The $4f'$ configuration of europium is confirmed by Eu-L_{III} X-ray absorption spectroscopy, showing only one maximum in the spectrum at the expected position of about 6980 eV. This value is by 8 eV smaller than observed for the standard Eu_2O_3 with electronic configuration $4f^6$ (Eu^{3+}).

Table 1. Data collection and handling.

Crystal:	gray platelet, size 0.020 × 0.050 × 0.070 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	717.2 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, φ/ω
$2\theta_{max}$:	67°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2129, 232
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 212
$N(param)_{refined}$:	11
Programs:	WinCSD [12], ATOMS [13]

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir(1)	2*a*	0	0	0	0.0084(4)	U_{11}	0.0068(5)	½U_{11}	0	0
Eu(1)	4*f*	⅔	⅓	0.55235(1)	0.0094(4)	U_{11}	0.0101(5)	½U_{11}	0	0
Ga(1)	6*h*	0.3178(5)	0.1589(2)	¼	0.0115(9)	0.0096(6)	0.0100(7)	½U_{11}	0	0

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